

The rheology of dense, polydisperse granular fluids under shear.

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The solution of the Enskog equation for the one-body velocity distribution of a moderately dense, arbitrary mixture of inelastic hard spheres undergoing planar shear flow is described. A generalization of the Grad moment method, implemented by means of a novel generating function technique, is used so as to avoid any assumptions concerning the size of the shear rate. The result is illustrated by using it to calculate the pressure, normal stresses and shear viscosity of a model polydisperse granular fluid in which grain size, mass and coefficient of restitution varies amongst the grains. The results are compared to a numerical solution of the Enskog equation as well as molecular dynamics simulations. Most bulk properties are well described by the Enskog theory and it is shown that the generalized moment method is more accurate than the simple (Grad) moment method. However, the description of the distribution of temperatures in the mixture predicted by Enskog theory does not compare well to simulation, even at relatively modest densities.

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Introduction

Granular systems under rapid flow can be modelled as a fluid of inelastic hard spheres for which a variety of theoretical and simulation methods may be used to explore and understand the rich phenomenology that they exhibit[1],[2],[3]. Of particular interest are sheared granular flows, in which the velocity in the direction of flow varies with position in an orthogonal direction, due to their practical relevance, accessibility to experiment and theoretical elegance. For a steady rate of shearing, such systems typically reach a steady state in which viscous heating, due to the shear, balances collisional cooling, due to the inelastic collisions, thus giving an example of a steady state nonequilibrium system. A number of papers have discussed the rheology of single component sheared granular fluids[4],[5],[6],[7] in which all particles are mechanically identical. However, all real fluids can be expected to contain a distribution of particle sizes and degrees of inelasticity. The purpose of this paper is to extend these studies to dense fluids composed of an arbitrary mixture of particle sizes and inelasticities.

The usual model for granular fluids consists of hard spheres which lose energy when they collide. Different models for the energy loss are possible and here, attention will be restricted to the simplest case in which the energy loss is proportional to the contribution to the kinetic energy of the normal velocities in the rest frame. This model is amenable to the same theoretical tools used to study elastic hard-sphere systems. In particular, it is possible to construct the exact Liouville equation describing the time evolution of the N-body distribution function[8],[9],[10] from which the Enskog and Boltzmann approximate kinetic equations follow. The latter are closed equations for the one-body distribution: the Enskog equation involves only the assumption of "molecular chaos"[11],[12], while the Boltzmann equation is its low-density limit. One of the attractions of the hard-sphere models is the existence of the Enskog equation which allows for the description of finite density fluids outside the domain of the validity of the Boltzmann equation. Since one of the purposes of the present work is to provide a foundation for the study of transport properties in realistic systems, the Enskog equation is used as a starting point. The price paid for this is that the results obtained must be evaluated numerically, but as discussed below, it is always possible, and quite trivial, to take the Boltzmann limit of the final expressions and to thereby proceed analytically in this special case.

The specific state studied here is that of uniform shear flow in which the flow is described by a velocity field $\vec{v}(\vec{r}) = \vec{a} \cdot \vec{r} = ay\hat{x}$ where a is the shear rate. As discussed below, this flow admits of a uniform state with spatially constant density and temperature. The shear rate, temperature and degree of inelasticity are related in the steady state by the requirement that the viscous heating and collisional cooling balance. Although the Enskog equation could be solved perturbatively in the shear rate, it is difficult to carry out the expansion to sufficiently high order to describe physically interesting effects such as normal stresses and shear thinning (although see ref.[5] where this is done for the Boltzmann equation). It is instead simpler to use a moment method without making any assumptions about the smallness of the shear rate as has been done for elastic hard spheres[13],[14] and for the Boltzmann equation for sheared binary fluids[15]. A similarly method that has been used is the so-called "Generalized Maxwellian" of Chou and Richman[6],[7]. In fact, as shown below, these two methods can actually be viewed as special

cases of a generalized moment expansion about an arbitrary Gaussian state.

An objection to using the moment method with the Enskog equation is that the calculations are technically difficult. In particular, the collision integrals which occur in the study of sheared fluids can be challenging to evaluate even in the case of the simpler Boltzmann theory (see, e.g. ref.[15]). One contribution of this work is to present a generating function technique which greatly simplifies the calculations. It is shown that all integrals of interest can be obtained by differentiating and taking appropriate limits of a single generating function which itself simply involves the evaluation of a few Gaussian integrals. With this technique, it is straightforward to evaluate all results for the most general case of differing particle sizes and coefficients of restitution in D -dimensions. The final results in fact turn out to be as simple in structure as the equivalent model of sheared single-component elastic hard spheres[13],[14].

A question which has aroused considerable interest is the degree to which mean-field theories, like the Enskog-Boltzmann kinetic theory, are applicable to granular systems[16]. This provides another reason for studying the particular case of USF as it is possible to simulate USF with the use of modified periodic boundaries by means of the Lees-Edwards simulation technique[17] so as to compare the approximate kinetic theory to numerical experiments. Furthermore, the Enskog equation may be solved numerically by means of the Direct Simulation Monte Carlo (DSMC) method[18]. Both methods are used here in order to elucidate the accuracy of the analytic calculations as a method of solving the Enskog equation and of the Enskog approximation itself compared to simulation.

The organization of this paper is as follows. In Section II, the Enskog theory is reviewed and the moment method for solving it is presented. It is shown how the moment method can be extended to allow for an arbitrary Gaussian reference state and the generating function formalism is introduced. The lowest non-trivial moment solutions of the Enskog equation are then described and used to calculate the pressure tensor for USF which thus describes the pressure, normal stresses and shear viscosity of the fluid in the steady state. In Section III, the solution of the moment equations is compared to DSMC and MD results for a model polydisperse fluid for a range of applied shear rates. The generalized moment method is shown to be superior to the simple (Grad) moment method and the Enskog theory is shown to give a good description of many rheological properties over a wide range of densities. However, the description of the distribution of temperatures as a function of grain size is shown to pose raising questions as to the accuracy of Enskog theory. The paper concludes with a discussion of the use and applicability of the results.

THEORY

Enskog approximation

Consider a system of N grains which are modeled as hard spheres. Each sphere is described by a position, \vec{q} , velocity, \vec{v} , and a species label r . A grain of species r has mass m_r while two grains of species r and s collide when they are separated by a distance σ_{rs} . This array of hard-sphere diameters may be specified arbitrarily but an important special case is that of additive hard sphere diameters wherein each species has a fixed diameter σ_r and $\sigma_{rs} = \frac{1}{2}(\sigma_r + \sigma_s)$. When grains i and j collide, their relative velocity after collision, $\vec{v}'_{ij} = \vec{v}'_i - \vec{v}'_j$ is given by

$$\vec{v}'_{ij} = \vec{v}_{ij} - (1 + \alpha_{r_i r_j}) \hat{q}_{ij} (\hat{q}_{ij} \cdot \vec{v}_{ij}) \quad (1)$$

where α_{rs} is the coefficient of restitution for collisions between grains of species r and s . The collisions are elastic if $\alpha_{rs} = 1$ while $\alpha_{rs} < 1$ leads to an irreversible loss of energy in each collision. Between collisions, the grains stream freely so that their velocities are constant. This model is a particular case of endothermic hard-sphere collisions in which the energy loss is proportional to the kinetic energy along the line of collision in the rest frame $E'_{ij} - E_{ij} = -\left(1 - \alpha_{r_i r_j}^2\right) \frac{1}{2} \mu_{r_i r_j} (\hat{q}_{ij} \cdot \vec{v}_{ij})^2$ where the reduced mass is $\mu_{rs} = m_r m_s / (m_r + m_s)$. Finally, it is useful to define the momentum exchange operator for any function of the relative velocities $g(\vec{v}_{ij})$ as

$$\hat{b}_{ij} g(\vec{v}_{ij}) = g(\vec{v}'_{ij}) = g(\vec{v}_{ij} - (1 + \alpha_{r_i r_j}) \hat{q}_{ij} (\hat{q}_{ij} \cdot \vec{v}_{ij})) \quad (2)$$

and all other velocities are left unchanged. Its inverse is

$$\hat{b}_{ij}^{-1} g(\vec{v}_{ij}) = g\left(\vec{v}_{ij} - \frac{1 + \alpha_{r_i r_j}}{\alpha_{r_i r_j}} \hat{q}_{ij} (\hat{q}_{ij} \cdot \vec{v}_{ij})\right). \quad (3)$$

The statistical properties of the system are determined by one and two body distribution functions, $f_r(\vec{q}, \vec{v}; t)$ and $f_{r_1 r_2}(\vec{q}_1, \vec{v}_1; \vec{q}_2, \vec{v}_2; t)$ respectively. The former gives the probability density to of finding a grain of species r

with the given position and velocity at time t and the latter gives the joint probability for two grains. The one-body distribution satisfies an exact equation (the first of the Born-Bogoliubov-Green-Kirkwood-Yvon (BBGKY) hierarchy)

$$\left(\frac{\partial}{\partial t} + \vec{v}_1 \cdot \frac{\partial}{\partial \vec{q}_1}\right) f_{r_1}(\vec{q}_1, \vec{v}_1; t) = - \sum_{r_1} \int d\vec{q}_2 d\vec{v}_2 \bar{T}_-(12) f_{r_1 r_2}(\vec{q}_1, \vec{v}_1; \vec{q}_2, \vec{v}_2; t) \quad (4)$$

where the binary collision operator is

$$\bar{T}_-(ij) = -\delta(q_{ij} - \sigma_{r_i r_j}) \left[\frac{1}{\alpha_{r_i r_j}} \hat{b}_{ij}^{-1} - 1 \right] \Theta(-\vec{v}_{ij} \cdot \hat{q}_{ij}) \vec{v}_{ij} \cdot \hat{q}_{ij} \quad (5)$$

where $\Theta(x) = 1$ if $x > 0$ and 0 otherwise. A similar equation relates the two-body distribution to the three body distribution, and so on. The Enskog approximation results from noting that the combination $\delta(q_{12} - \sigma_{r_1 r_2}) \Theta(-\vec{v}_{12} \cdot \hat{q}_{12}) f_{r_1 r_2}(\vec{q}_1, \vec{v}_1; \vec{q}_2, \vec{v}_2; t)$ picks out the pre-collisional part of the distribution and assuming that, *prior to collision and at the moment of contact*, the grains are uncorrelated. The specific assumption is that

$$\begin{aligned} & \delta(q_{12} - \sigma_{r_1 r_2}) \Theta(-\vec{v}_{12} \cdot \hat{q}_{12}) f_{r_1 r_2}(\vec{q}_1, \vec{v}_1; \vec{q}_2, \vec{v}_2; t) \\ & \simeq \delta(q_{12} - \sigma_{r_1 r_2}) \Theta(-\vec{v}_{12} \cdot \hat{q}_{12}) f_{r_1}(\vec{q}_1, \vec{v}_1; t) f_{r_2}(\vec{q}_2, \vec{v}_2; t) \chi_{r_1 r_2}(\vec{q}_1, \vec{q}_2; t) \end{aligned} \quad (6)$$

where the term $\chi_{r_1 r_2}(\vec{q}_1, \vec{q}_2; t)$, the spatial pair distribution function (pdf), accounts for spatial correlations as exist even in equilibrium. If it is taken to be the local-equilibrium functional of the nonequilibrium densities then the approximation is completely specified and is known as the Generalized Enskog Approximation[19].

Hydrodynamic fields

The local hydrodynamic fields of partial number densities $n_r(\vec{q}, t)$, local velocity $\vec{u}(\vec{q}, t)$, and temperature $T(\vec{q}, t)$ are defined as

$$\begin{aligned} n_r(\vec{q}, t) &= \int d\vec{v} f_r(\vec{q}, \vec{v}; t) \\ \rho(\vec{q}, t) \vec{u}(\vec{q}, t) &= \sum_r \int d\vec{v} m_r \vec{v} f_r(\vec{q}, \vec{v}; t) \\ \frac{D}{2} k_B T(\vec{q}, t) &= \sum_r \int d\vec{v} \frac{1}{2} m_r v^2 f_r(\vec{q}, \vec{v}; t) \end{aligned} \quad (7)$$

where $\rho(\vec{q}, t) = \sum_r m_r n_r(\vec{q}, t)$ is the total mass density, D is the dimensionality of the system and k_B is Boltzmann's constant. The exact time evolution of these fields follows from Eq.(4) which gives[10]

$$\begin{aligned} \frac{\partial}{\partial t} n_r + \vec{\nabla} \cdot (\vec{u} n_r) + \vec{\nabla} \cdot \vec{j}_r^K &= 0 \\ \frac{\partial}{\partial t} \vec{u} + \vec{u} \cdot \vec{\nabla} \vec{u} + \rho^{-1} \vec{\nabla} \cdot \vec{P} &= 0 \\ \left(\frac{\partial}{\partial t} + \vec{u} \cdot \vec{\nabla} \right) T - \frac{T}{n} \vec{\nabla} \cdot \sum_l \vec{j}_l^K + \frac{2}{D n k_B} [\vec{P} : \vec{\nabla} \vec{u} + \vec{\nabla} \cdot \vec{q}] &= \frac{2}{D n k_B} \xi \end{aligned} \quad (8)$$

with the number current

$$\vec{j}_r^K = \int d\vec{v}_1 f_r(\vec{r}, \vec{v}_1, t) \vec{V}_1 \quad (9)$$

where $\vec{V}_1 = \vec{v}_1 - \vec{u}(\vec{q}_1, t)$, the pressure tensor $\vec{P} = \vec{P}^K + \vec{P}^V$ with kinetic and collisional contributions

$$\begin{aligned} \vec{P}^K(\vec{r}, t) &= \sum_r m_r \int d\vec{v}_1 f_r(\vec{r}, \vec{v}_1, t) \vec{V}_1 \vec{V}_1 \\ \vec{P}^V(\vec{r}, t) &= \frac{1}{4} \sum_{r_1 r_2} \mu_{r_1 r_2} (1 + \alpha_{r_1 r_2}) \int dx_1 dx_2 \hat{q}_{12} \vec{q}_{12} (\hat{q}_{12} \cdot \vec{v}_{12})^2 \delta(q_{12} - \sigma_{l_1 l_2}) \Theta(-\hat{q}_{12} \cdot \vec{v}_{12}) \\ &\quad \times f_{r_1 r_2}(x_1, x_2; t) \int_0^1 dx \delta(\vec{r} - x \vec{q}_1 - (1-x) \vec{q}_2), \end{aligned} \quad (10)$$

the heat flux vector $\vec{q} = \vec{q}^K + \vec{q}^V + \vec{q}^{\delta E}$ with

$$\begin{aligned}\vec{q}^K(\vec{r}, t) &= \sum_r \frac{1}{2} m_r \int d\vec{v}_1 f_r(\vec{r}, \vec{v}_1, t) \vec{V}_1 V_1^2 \\ \vec{q}^V(\vec{r}, t) &= \frac{1}{2} \sum_{r_1 r_2} \mu_{r_1 r_2} (1 + \alpha_{r_1 r_2}) \int dx_1 dx_2 \vec{q}_{12} (\hat{q}_{12} \cdot \vec{v}_{12})^2 \delta(q_{12} - \sigma_{l_1 l_2}) \Theta(-\hat{q}_{12} \cdot \vec{v}_{12}) \\ &\quad \times f_{r_1 r_2}(x_1, x_2; t) \left(\vec{V} - \vec{u}(\vec{q}_1, t) \right) \cdot \hat{q}_{12} \int_0^1 dx \delta(\vec{r} - x \vec{q}_1 - (1-x) \vec{q}_2) \\ \vec{q}^{\delta E}(\vec{r}, t) &= -\frac{1}{4} \sum_{r_1 r_2} \left(1 - \alpha_{r_1 r_2}^2 \right) \frac{1}{2} \mu_{r_1 r_2} \frac{m_{r_1} - m_{r_2}}{m_{r_1} + m_{r_2}} \int dx_1 dx_2 \vec{q}_{12} (\hat{q}_{12} \cdot \vec{v}_{12})^3 \delta(q_{12} - \sigma_{l_1 l_2}) \Theta(-\hat{q}_{12} \cdot \vec{v}_{12}) \\ &\quad \times f_{r_1 r_2}(x_1, x_2; t) \int_0^1 dx \delta(\vec{r} - x \vec{q}_1 - (1-x) \vec{q}_2)\end{aligned}\tag{11}$$

where the center of mass velocity $\vec{V} = \frac{m_{r_1} \vec{v}_1 + m_{r_2} \vec{v}_2}{m_{r_1} + m_{r_2}}$, and the energy sink term

$$\begin{aligned}\xi(\vec{r}, t) &= \frac{1}{4} \sum_{r_1 r_2} \left(1 - \alpha_{r_1 r_2}^2 \right) \mu_{r_1 r_2} \int dx_1 dx_2 (\vec{q}_{12} \cdot \vec{v}_{12})^3 \delta(q_{12} - \sigma_{l_1 l_2}) \Theta(-\hat{q}_{12} \cdot \vec{v}_{12}) \\ &\quad \times f_{r_1 r_2}(x_1, x_2; t) \delta(\vec{r} - \vec{q}_1),\end{aligned}\tag{12}$$

Using the approximation given in Eq.(6) gives expressions for the fluxes and the heat sink which only require knowledge of the one-body distribution function.

Uniform Shear Flow

The Enskog equation is indeterminate until some boundary condition is specified. If periodic boundary conditions are imposed, then it is easy to see that the Enskog equation admits of a spatially homogeneous solution which is, however, time-dependent due to the cooling resulting from the dissipative collisions. This is the well known Homogeneous Cooling State (HCS). Uniform Shear Flow (USF) is another simple nonequilibrium state supported by this system. In USF, the density and temperature are spatially homogeneous while the velocity field varies linearly with position, viz $\vec{u}(\vec{r}) = \vec{a} \cdot \vec{r}$ where the shear tensor, \vec{a} , will be taken to be $a\hat{x}\hat{y}$ in a Cartesian coordinate system. There is therefore a flow in the x-direction which varies linearly in the y-direction. We hypothesize that in this case the distribution will only depend on the peculiar velocity $f_r(\vec{q}, \vec{v}; t) = f_r(\vec{V} = \vec{v} - \vec{a} \cdot \vec{q}; t)$. The Enskog equation then becomes

$$\left(\frac{\partial}{\partial t} - \vec{V}_1 \cdot \vec{a}^T \cdot \frac{\partial}{\partial \vec{V}_1} \right) f_{r_1}(\vec{V}_1; t) = - \sum_{r_2} \int d\vec{q}_2 d\vec{v}_2 \bar{T}_- (12) f_{r_1}(\vec{V}_1; t) f_{r_2}(\vec{V}_2; t) \chi_{r_1 r_2}(\vec{q}_1, \vec{q}_2; t). \tag{13}$$

In fact, the linear flow field is the only one that makes the collisional term on the right independent of position as follows from the observation that it will be independent of position only if $\vec{u}(\vec{q}_1) - \vec{u}(\vec{q}_2)$ is a function of \vec{q}_{12} . (The function $\chi_{r_1 r_2}(\vec{q}_1, \vec{q}_2; t)$, evaluated in the local equilibrium approximation, will only depend on \vec{q}_{12} if the density is uniform.) In fact, the requirement that $\vec{u}(\vec{q}_1) - \vec{u}(\vec{q}_2) = \vec{U}(\vec{q}_{12})$ for some field $\vec{U}(\vec{q}_{12})$ is only satisfied for $\vec{U}(\vec{q}_{12}) = \vec{u}(\vec{q}_{12})$ (demonstrated by take $\vec{q}_2 = \vec{0}$). One must also have that $\vec{u}(\vec{q}_1)$ is odd, as shown by reversing the arguments, and that $\vec{u}\left(\frac{p}{q}\vec{q}_1\right) = \frac{p}{q}\vec{u}(\vec{q}_1)$, for arbitrary integers p and q , as follows by iterating with $\vec{q}_2 = -\vec{q}_1$. The only continuous function satisfying these constraints is one linear in \vec{q}_1 , which is to say USF.

Another consequence of the assumption of a uniform state is that the density and temperature are spatially uniform and it may be verified that the pressure tensor, heat-flux vector, number flux and heating rate are all spatially uniform as well. The equations for the hydrodynamic fields then become

$$\begin{aligned}\frac{\partial}{\partial t} n_r &= 0 \\ \frac{\partial}{\partial t} \vec{u} &= 0 \\ \frac{\partial}{\partial t} T + \frac{2}{Dn k_B} \vec{P} : \vec{a} &= \frac{2}{Dn k_B} \xi\end{aligned}\tag{14}$$

which shows that the hydrodynamic fields will also be independent of time if the viscous heating, characterized by the second term on the left in the temperature equation, balances the cooling described by the source term on the right. It is therefore consistent to hypothesize not only a spatially uniform solution to the Enskog equation, but that a time-independent solution exists. In this steady state, the only two quantities having the units of time are the temperature and the shear rate. It will therefore be the case that the relevant dimensionless control parameter is $a^* = a \sqrt{\frac{\langle m \rangle \langle \sigma \rangle^2}{k_B T}}$, where the average diameter is $\langle \sigma \rangle = \sum_{rs} x_r x_s \sigma_{rs}$ and the average mass is $\langle m \rangle = \sum_r x_r m_r$. For a given set of material parameters, the steady state will be unique in that the value of a^* as determined from eq.(14) will be independent of the shear rate a applied through the Lees-Edwards boundary conditions: in other words, for a given value of a the temperature will relax to a value such that the same value of a^* is always achieved.

Does this mean that once the fluid is moving according to the linear velocity profile, it will continue to do so forever? The answer is that it depends on the boundary conditions which have so far not been specified. The steady-state distribution hypothesized, and the sustained USF it implies, is only possible if the distribution function is compatible with some set of boundary conditions. For example, if the system is bounded with rigid moving walls, then the final distribution will depend on the detailed dynamics of collisions of grains with the wall. Here, however, we will assume the imposition of Lees-Edwards boundary conditions which are periodic boundaries in the co-moving frame. A time-independent, spatially homogeneous distribution function is in fact compatible with these boundary conditions and they are also amenable to application in molecular dynamics computer simulations, as discussed in more detail below.

Before turning to the construction of a spatially uniform, time-independent solution of the Enskog equation, some comments can be made about the generality of these results. First, the only properties of the flow state used so far are that the flow field is a linear function of the coordinate and that the shear tensor satisfies $\overleftrightarrow{a} \cdot \overleftrightarrow{a} = 0$ (needed to convert the spatial derivative on the left in Eq.(4) into a velocity derivative in Eq.(13)). Second, the Boltzmann equation results from taking the lowest order term in an expansion of the integral in Eq.(13) in terms of the hard-sphere diameter. This results in the replacement of $\overrightarrow{v}_{12} \rightarrow \overrightarrow{V}_{12}$ so that, in this approximation, the collision integral is independent of position for any choice of the flow field.

MOMENT SOLUTIONS TO THE ENSKOG EQUATION

Moment Expansion

In order to develop an approximate solution of the Enskog equation without making any restrictive assumptions about the size of either the shear rate or the degree of inelasticity, the distribution function is expanded in a complete set of polynomials about some suitable reference state[20],[21]. Here, more generally than is usually done, the reference state will be taken to be an arbitrary Gaussian so that the expansion takes the form

$$f_r(\overrightarrow{V}; \{n_s\}, T) = n_r \det(\overleftrightarrow{\Gamma})^{1/2} \pi^{-D/2} \exp(-\overrightarrow{V} \cdot \overleftrightarrow{\Gamma}^r \cdot \overrightarrow{V}) \left(\sum_{n=0} \frac{1}{n!} \sum_{I_n} A_{I_n}^r H_{I_n}(\sqrt{2} \overleftrightarrow{\Gamma}^{r1/2} \cdot \overrightarrow{V}) \right) \quad (15)$$

where $\overleftrightarrow{\Gamma}^r$ is a positive-definite, real, symmetric matrix and an abbreviated notation is used whereby $I_n \equiv i_1 \dots i_n$. As such, it can be written, via Cholesky decomposition, as $\overleftrightarrow{\Gamma}^r = \overleftrightarrow{\Gamma}^{r1/2} \cdot (\overleftrightarrow{\Gamma}^{r1/2})^T$ for some matrix $\overleftrightarrow{\Gamma}^{r1/2}$. The functions used in the expansion are the Hermite polynomials[21] given by

$$H_{I_n}(\overrightarrow{c}) = (-1)^n e^{c^2/2} \frac{\partial}{\partial c_{i_1}} \dots \frac{\partial}{\partial c_{i_n}} e^{-c^2/2} \quad (16)$$

so that, e.g., $H_{ij}(\overrightarrow{c}) = c_i c_j - \delta_{ij}$. They are orthonormal in D -dimensions because

$$\left(\frac{1}{2\pi} \right)^{D/2} \int d\overrightarrow{c} e^{-c^2/2} H_{I_n}(\overrightarrow{c}) H_{J_m}(\overrightarrow{c}) = \delta_{mn} \sum_{P(j_1 j_2 \dots j_m)} \delta_{i_1 j_1} \dots \delta_{i_n j_n}. \quad (17)$$

so that the coefficients of the expansion are related to the velocity moments via

$$\int d\overrightarrow{V} f_r(\overrightarrow{V}; \{n_s\}, T) H_{I_n}^r(\overrightarrow{c}_r) = n_r A_{I_n}^r \quad (18)$$

where $\vec{C}_r = \sqrt{2} \overleftrightarrow{\Gamma}^{r1/2} \cdot \vec{V}$. Evaluating equation (7) relates the lower order coefficients to the hydrodynamic fields as

$$\begin{aligned} n_r(\vec{q}, t) &= n_r A^r \\ \rho(\vec{q}, t) u_i(\vec{q}, t) &= \sum_r m_r n_r A^r u_i + \sum_r \sum_j m_r n_r \left(\sqrt{2} \overleftrightarrow{\Gamma}^{r1/2} \right)_{ij}^{-1} A_j^r \\ Dn k_B T &= \frac{1}{2} \sum_r \left(m_r n_r Tr \left(\left(\overleftrightarrow{\Gamma}^r \right)^{-1} \right) + m_r n_r Tr \left(\left(\overleftrightarrow{\Gamma}^r \right)^{-1/2} \cdot \overleftrightarrow{A}^r \cdot \left(\overleftrightarrow{\Gamma}^{rT} \right)^{-1/2} \right) \right) \end{aligned} \quad (19)$$

implying $A^r = 1$ and $\sum_r \sum_j m_r n_r \left(\sqrt{2} \overleftrightarrow{\Gamma}^{r1/2} \right)_{ij}^{-1} A_j^r = 0$. The kinetic contribution to the stress tensor is

$$P_{ij}^K = \sum_r m_r \int d\vec{V} f_r(\vec{V}; \{n_s\}, T) V_i V_j = \frac{1}{2} \sum_r m_r n_r \left(\left(\overleftrightarrow{\Gamma}^r \right)^{-1/2} \cdot \left(\vec{1} + \overleftrightarrow{A}^r \right) \cdot \left(\overleftrightarrow{\Gamma}^{rT} \right)^{-1/2} \right)_{ij}. \quad (20)$$

Each species has a temperature given by

$$Dn_r k_B T_r = m_r \int d\vec{V} f_r(\vec{V}; \{n_s\}, T) V^2 = \frac{1}{2} \left(m_r n_r Tr \left(\left(\overleftrightarrow{\Gamma}^r \right)^{-1} \right) + m_r n_r Tr \left(\left(\overleftrightarrow{\Gamma}^r \right)^{-1/2} \cdot \overleftrightarrow{A}^r \cdot \left(\overleftrightarrow{\Gamma}^{rT} \right)^{-1/2} \right) \right). \quad (21)$$

Calculation of the velocity moments of Eq.(15) shows that there are actually redundant degrees of freedom in the sense that any change in $\overleftrightarrow{\Gamma}^r$ can always be compensated by changes in the coefficients of the expansion. These redundant degrees of freedom can most conveniently be eliminated by restricting the form of either $\overleftrightarrow{\Gamma}^r$ or $A_{I_2}^r$ although one could imagine applying the restrictions to higher moments. There are two cases of particular interest. In the first, $\overleftrightarrow{\Gamma}$ is left unspecified and we set $A_{i_1 i_2}^r = 0$ so that all information about the second moments comes from the Gaussian. This will be referred to below as the Generalized Moment Expansion or GME. In the second case, $\overleftrightarrow{\Gamma}$ is specialized to a diagonal matrix by setting

$$\overleftrightarrow{\Gamma}^r = \frac{m_r}{2k_B T_r} \vec{1} \quad (22)$$

where the parameters T_r are to be determined. In this case, only the trace of the second order coefficients is set to zero so that

$$\sum_i A_{ii}^r = 0. \quad (23)$$

This represents an expansion about a local equilibrium state in which the temperatures of the different species are allowed to vary and will be referred to below as the Simple Moment Expansion or SME. Further trade-offs between the degrees of freedom in the reference state and those in the moment expansion are possible, but do not appear to offer any qualitative advantages. For example, one could use the restrictions

$$\begin{aligned} \overleftrightarrow{\Gamma}^r &= \frac{m_r}{2k_B T} \vec{1} \\ \sum_r \sum_i A_{ii}^r &= 0 \end{aligned} \quad (24)$$

so that the reference state is simple equilibrium. This possibility will not be considered here, although there is nothing to rule it out in principle. Note that in no case can we force the temperatures of the subspecies to be equal since that would eliminate certain degrees of freedom altogether and this would lead to inconsistencies when we use the expansion to solve the Enskog equation.

Substituting the general expansion given in Eq.(15) into the Enskog equation, multiplying by $H_{I_n}^{r1} \left(\sqrt{2} \overleftrightarrow{\Gamma}^{r1/2} \cdot \vec{V}_1 \right)$ and integrating over velocities yields an infinite hierarchy of coupled equations for the moments which are given explicitly in the appendix. The n -th order approximation is usually taken to consist of truncating the expansion in Eq.(15) to the first n terms and using the first n equations of this hierarchy to determine the moments. The remainder of this paper will focus on the simplest nontrivial approximations, which are in both cases the second order approximation. For the GME, some simplification allows the moment approximation to be written as

$$\frac{\partial \Gamma_{i_1 i_2}^{r1-1}}{\partial t} + a \left(\Gamma_{y i_2}^{r1-1} \delta_{i_1 x} + \Gamma_{y i_1}^{r1-1} \delta_{i_2 x} \right) = \sum_{r_2} n_{r_2} \chi_{r_1 r_2} E_{i_1 i_2}^{r_1 r_2} \quad (25)$$

with

$$E_{i_1 i_2}^{r_1 r_2} = -2\pi^{-D} \det \left(\overleftrightarrow{\Gamma}^{r_1} \overleftrightarrow{\Gamma}^{r_2} \right)^{1/2} \int d\vec{V}_1 d\vec{V}_2 d\vec{q}_2 V_{1i_1} V_{1i_2} \overline{T}_-(12) \exp \left(-\vec{V}_1 \cdot \overleftrightarrow{\Gamma}^{r_1} \cdot \vec{V}_1 - \vec{V}_2 \cdot \overleftrightarrow{\Gamma}^{r_1} \cdot \vec{V}_2 \right) \quad (26)$$

and where $\chi_{r_1 r_2} \equiv \chi_{r_1 r_2}(\vec{q}_1, \vec{q}_1 + \sigma_{rs} \hat{q}_{12}; t)$ is independent of \vec{q}_1 and \hat{q}_{12} in a homogeneous system. This system of equations suffices to determine the matrices $\overleftrightarrow{\Gamma}^{r_1}$. For a given applied shear rate a , the steady-state temperature, and hence the dimensionless shear rate a^* , is then determined from the second moments from Eq.(19). Explicitly, the temperature is $T = \sum_r x_r T_r$ where the partial temperatures are given by

$$Dk_B T_r = \frac{m_r}{2} T_r \left(\left(\overleftrightarrow{\Gamma}^{r_1} \right)^{-1} \right). \quad (27)$$

This lowest order GME corresponds to the "Generalized Maxwellian" approximation of Chou et al[6],[7]. For the SME, the moment equations are

$$\begin{aligned} & \frac{\partial}{\partial t} A_{i_1 i_2}^{r_1} + \frac{\partial \ln T_{r_1}}{\partial t} (A_{i_1 i_2}^{r_1} + \delta_{i_1 i_2}) + a (\delta_{x i_1} A_{i_2 y}^{r_1} + \delta_{x i_2} A_{i_1 y}^{r_1} + \delta_{x i_1} \delta_{i_2 y} + \delta_{x i_2} \delta_{i_1 y}) \\ &= \sum_{r_2} n_{r_2} \chi_{r_1 r_2} \left[B_{i_1 i_2}^{r_1 r_2} + \frac{1}{2} \sum_{j_1 j_2} (C_{i_1 i_2, j_1 j_2}^{r_1 r_2} A_{j_1 j_2}^{r_1} + D_{i_1 i_2, j_1 j_2}^{r_1 r_2} A_{j_1 j_2}^{r_2}) \right] \\ T_r \left(\overleftrightarrow{A}^{r_1} \right) &= 0 \end{aligned} \quad (28)$$

with

$$\begin{aligned} B_{i_1 i_2}^{r_1 r_2} &= - \int d\vec{V}_1 d\vec{V}_2 d\vec{q}_2 H_{i_1 i_2}(\vec{C}_1) \overline{T}_-(12) \Phi_{r_1}(\vec{V}_1; T_{r_1}) \Phi_{r_2}(\vec{V}_2; T_{r_2}) \\ C_{i_1 i_2, j_1 j_2}^{r_1 r_2} &= - \int d\vec{V}_1 d\vec{V}_2 d\vec{q}_2 H_{i_1 i_2}(\vec{C}_1) \overline{T}_-(12) \Phi_{r_1}(\vec{V}_1; T_{r_1}) H_{j_1 j_2}(\vec{C}_1) \Phi_{r_2}(\vec{V}_2; T_{r_2}) \\ D_{i_1 i_2, j_1 j_2}^{r_1 r_2} &= - \int d\vec{V}_1 d\vec{V}_2 d\vec{q}_2 H_{i_1 i_2}(\vec{C}_1) \overline{T}_-(12) \Phi_{r_1}(\vec{V}_1; T_{r_1}) \Phi_{r_2}(\vec{V}_2; T_{r_2}) H_{j_1 j_2}(\vec{C}_2) \\ \vec{C}_j &= \left(\frac{m_{r_j}}{k_B T_{r_j}} \right)^{1/2} \vec{V}_j. \\ \Phi_r(\vec{V}_1; T_r) &= \left(\frac{m_r}{2k_B T_r \pi} \right)^{D/2} \exp \left(-\frac{m_r}{2k_B T_r} V_1^2 \right) \end{aligned} \quad (29)$$

The first of Eqs.(28) are a set of linear equations for the coefficients $A_{i_1 i_2}^{r_1}$ whereas the second can be thought of as a set of constraints that serve to determine the partial temperatures.

Finally, one problem with the moment expansion in general is that the truncated distributions are not necessarily positive definite. An ad hoc procedure to rectify this problem is to resum the truncated moment expansion so that one writes, in the general case,

$$\begin{aligned} f_r(\vec{V}; \{n_s\}, T) &= n_r \det \left(\overleftrightarrow{\Gamma} \right)^{1/2} \pi^{-D/2} \exp \left(-\vec{V} \cdot \overleftrightarrow{\Gamma}^r \cdot \vec{V} \right) \left(1 + \sum_n \frac{1}{n!} \sum_{I_n} \overline{A}_{I_n}^r H_{I_n} \left(\sqrt{2} \overleftrightarrow{\Gamma}^{r1/2} \cdot \vec{V} \right) \right) \\ &= n_r Z^{-1} \pi^{-D/2} \exp \left(-\vec{V} \cdot \overleftrightarrow{\Gamma}^r \cdot \vec{V} + \sum_n \frac{1}{n!} \sum_{I_n} \overline{A}_{I_n}^r H_{I_n} \left(\sqrt{2} \overleftrightarrow{\Gamma}^{r1/2} \cdot \vec{V} \right) \right) \end{aligned} \quad (30)$$

where the new coefficients $\overline{A}_{I_n}^r$ are chosen so that the two series agree, term by term, up to the desired order. In general, the normalization constant Z must also be determined. For the second order GME, this is not an issue since the approximate distribution is Gaussian. For the SME, one has that

$$\begin{aligned} f_r(\vec{V}; \{n_s\}, T) &\simeq n_r \left(\frac{m_r}{2k_B T_r} \right)^{D/2} \pi^{-D/2} \exp \left(-\frac{m_r}{2k_B T_r} V^2 \right) \left(1 + \frac{1}{2!} \sum_{i_1 i_2} \overline{A}_{i_1 i_2}^r H_{i_1 i_2} \left(\sqrt{2} \overleftrightarrow{\Gamma}^{r1/2} \cdot \vec{V} \right) \right) \\ &\simeq n_r \det \left(\overleftrightarrow{\Gamma} + \overleftrightarrow{A}^r \right)^{-1/2} \pi^{-D/2} \exp \left(-\frac{m_r}{2k_B T_r} \sum_{i_1 i_2} \vec{V} \cdot \left(\overleftrightarrow{\Gamma} + \overleftrightarrow{A}^r \right)^{-1} \cdot \vec{V} \right) \end{aligned} \quad (31)$$

which is structurally the same as the GME except that the matrix of second moments is determined through the linearized equations (28)-(29). Thus, in this formulation, the second order GME and SME are virtually identical except for the approximations used to determine the second moments.

Generating Function for Collision Integrals

All of the collision integrals that will be needed can be obtained from the generating function

$$Z_{I_n}^{r_1 r_2} = -\pi^{-D} \int d\vec{V}_1 d\vec{V}_2 d\vec{q}_2 \left(\prod_{j=1}^n (\vec{q}_{12})_{i_j} \right) \exp(\vec{\Lambda} \cdot \vec{V}_1) \bar{T}_-(12) \exp(-\vec{V}_1 \cdot \overleftarrow{\Gamma}^{r_1} \cdot \vec{V}_1 - \vec{V}_2 \cdot \overleftarrow{\Gamma}^{r_2} \cdot \vec{V}_2) \quad (32)$$

by differentiating with respect to the matrices $\Gamma_{ij}^{r_1}$ and $\Gamma_{ij}^{r_2}$ and the vector Λ_i and taking appropriate limits (such as $\vec{\Lambda} \rightarrow 0$). For example, by inspection, one has that

$$\begin{aligned} E_{i_1 i_2}^{r_1 r_2} &= 2 \det(\overleftarrow{\Gamma}^{r_1} \overleftarrow{\Gamma}^{r_2})^{1/2} \lim_{\vec{\Lambda} \rightarrow 0} \frac{\partial^2}{\partial \Lambda_{i_1} \partial \Lambda_{i_2}} Z^{r_1 r_2} \\ B_{i_1 i_2}^{r_1 r_2} &= \frac{m_{r_1}}{2k_B T_{r_1}} \lim_{\overleftarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x} \overleftarrow{\Gamma}} E_{i_1 i_2}^{r_1 r_2} \\ C_{i_1 i_2, j_1 j_2}^{r_1 r_2} &= -\frac{m_{r_1}}{2k_B T_{r_1}} \lim_{\overleftarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x} \overleftarrow{\Gamma}} \det(\overleftarrow{\Gamma}^{r_1} \overleftarrow{\Gamma}^{r_2})^{1/2} \left(\frac{m_{r_1}}{k_B T_{r_1}} \frac{\partial}{\partial \Gamma_{i_1 j_2}^{r_1}} + \delta_{j_1 j_2} \right) \lim_{\vec{\Lambda} \rightarrow 0} \frac{\partial^2}{\partial \Lambda_{i_1} \partial \Lambda_{i_2}} Z^{r_1 r_2} \\ &= -\frac{1}{2} \left(\frac{m_{r_1}}{k_B T_{r_1}} \right)^2 \lim_{\overleftarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x} \overleftarrow{\Gamma}} \frac{\partial}{\partial \Gamma_{j_1 j_2}^{r_1}} E_{i_1 i_2}^{r_1 r_2} \\ D_{i_1 i_2, j_1 j_2}^{r_1 r_2} &= -\frac{m_{r_1}}{2k_B T_{r_1}} \frac{m_{r_2}}{k_B T_{r_2}} \lim_{\overleftarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x} \overleftarrow{\Gamma}} \frac{\partial}{\partial \Gamma_{j_1 j_2}^{r_2}} E_{i_1 i_2}^{r_1 r_2} \end{aligned} \quad (33)$$

while comparison of Eqs.(10), evaluated for a uniform system, and (67) the collisional contribution to the pressure is found to be

$$P_{i_1 i_2}^V = \frac{1}{4} \sum_{r_1 r_2} n_{r_1} n_{r_2} \chi_{r_1 r_2} \det(\overleftarrow{\Gamma}^{r_1} \overleftarrow{\Gamma}^{r_2})^{1/2} m_{r_1} \lim_{\vec{\Lambda} \rightarrow 0} \frac{\partial}{\partial \Lambda_{i_2}} Z_{i_1}^{r_1 r_2}. \quad (34)$$

The generating function is shown in appendix to be

$$Z_{I_n}^{r_1 r_2} = \frac{1}{2} \det(\overleftarrow{\Gamma}^{r_1} \overleftarrow{\Gamma}^{r_2})^{-1/2} \sigma_{r_1 r_2}^{D-1} \int d\hat{q} \left(\prod_{j=1}^n \sigma_{r_1 r_2} \hat{q}_{i_j} \right) \left[\tilde{Z}^{r_1 r_2} \left((1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} \right) - \tilde{Z}^{r_1 r_2}(0) \right] \quad (35)$$

with

$$\begin{aligned} \tilde{Z}^{r_1 r_2}(x) &= X_{r_1 r_2} F_1 \left(\frac{2w_{r_1 r_2} + \vec{\Lambda} \cdot \overleftarrow{\Gamma}^{r_1-1} \cdot \hat{q}_{12}}{2X_{r_1 r_2}} - \frac{1}{2} x (\vec{\Lambda} \cdot \hat{q}) X_{r_1 r_2} \right) \\ &\quad \times \exp \left(\frac{1}{4} \vec{\Lambda} \cdot \overleftarrow{G}^{r_1 r_2}(x) \cdot \vec{\Lambda} - x w_{r_1 r_2} \vec{\Lambda} \cdot \hat{q} \right) \\ F_n(x) &= -\frac{2}{\sqrt{\pi}} \int_{-\infty}^{-x} (u+x)^n \exp(-u^2) du \\ X_{r_1 r_2} &= \sqrt{\hat{q} \cdot (\overleftarrow{\Gamma}^{r_1-1} + \overleftarrow{\Gamma}^{r_2-1}) \cdot \hat{q}} \\ \overleftarrow{G}^{r_1 r_2}(x) &= \overleftarrow{\Gamma}^{r_1-1} + 2(\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2})^{-1} - 2x \overleftarrow{\Gamma}^{r_1-1} \cdot \hat{q} \hat{q} + x^2 X_{r_1 r_2}^2 \hat{q} \hat{q} \\ w_{r_1 r_2} &= \sigma_{r_1 r_2} \hat{q} \cdot \overleftarrow{a} \cdot \hat{q} \end{aligned} \quad (36)$$

and, in particular

$$\begin{aligned} F_0(x) &= \operatorname{erf}(x) - 1 \\ F_1(x) &= \frac{1}{\sqrt{\pi}} e^{-x^2} + x(\operatorname{erf}(x) - 1). \end{aligned} \quad (37)$$

(The Appendix also discusses the general case of an arbitrary flow state.) The elements needed for the second order moment equations are worked out in Appendix where it is shown that

$$\begin{aligned} E_{i_1 i_2}^{r_1 r_2} &= -\sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} \int d\hat{q} X_{r_1 r_2} F_1 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \left[\left(\vec{\Gamma}^{r_1-1} \cdot \hat{q} \right)_{i_1} \hat{q}_{i_2} + \left(\vec{\Gamma}^{r_1-1} \cdot \hat{q} \right)_{i_2} \hat{q}_{i_1} \right] \\ &\quad + \frac{1}{2} \sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2})^2 \left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \right)^2 \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} X_{r_1 r_2}^3 \left[\left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) F_0 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) + F_1 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \left(2 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right)^2 + 2 \right) \right] \end{aligned} \quad (38)$$

from which immediately follows the coefficients for the simple moment approximation

$$\begin{aligned} B_{i_1 i_2}^{r_1 r_2} &= -2\sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2} Y_{r_1 r_2}}{m_{r_1}} \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} F_1 \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right) \\ &\quad + \frac{1}{4} \sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2})^2 \left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \right)^2 Y_{r_1 r_2}^3 \frac{m_{r_1}}{k_B T_{r_1}} \\ &\quad \times \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} \left[\left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right) F_0 \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right) + F_1 \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right) \left(2 \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right)^2 + 2 \right) \right] \\ C_{i_1 i_2, j_1 j_2}^{r_1 r_2} &= \frac{T_{r_1}}{T_{r_2}} \frac{m_{r_2}}{m_{r_1}} D_{i_1 i_2, j_1 j_2}^{r_1 r_2} - 2\sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2} Y_{r_1 r_2}}{m_{r_1}} \int d\hat{q} (\delta_{i_1 j_1} \hat{q}_{i_2} \hat{q}_{j_2} + \delta_{i_2 j_1} \hat{q}_{i_1} \hat{q}_{j_2}) F_1 \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right) \\ D_{i_1 i_2, j_1 j_2}^{r_1 r_2} &= -4\sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2} Y_{r_1 r_2}^{-1}}{m_{r_1}} \left(\frac{k_B T_{r_2}}{m_{r_2}} \right) \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} \hat{q}_{j_1} \hat{q}_{j_2} \left(F_1 \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right) - \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right) F_0 \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right) \right) \\ &\quad + 3\sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2})^2 \left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \right)^2 \frac{m_{r_1}}{k_B T_{r_1}} \left(\frac{k_B T_{r_2}}{m_{r_2}} \right) Y_{r_1 r_2} \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} \hat{q}_{j_1} \hat{q}_{j_2} F_1 \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right) \end{aligned} \quad (39)$$

where

$$Y_{r_1 r_2} = \sqrt{2 \frac{k_B T_{r_1}}{m_{r_1}} + 2 \frac{k_B T_{r_2}}{m_{r_2}}}. \quad (40)$$

which, together with Eqs.(28), Eq.(25), Eq.(21) and the requirement that $\sum_r n_r T_r = nT$ complete the specification of the second-order moment approximations. The collisional contribution to the pressure is

$$P_{i_1 i_2}^V = -\frac{1}{8} \sum_{r_1 r_2} n_{r_1} n_{r_2} \sigma_{r_1 r_2}^D \chi_{r_1 r_2} (1 + \alpha_{r_1 r_2}) \mu_{r_1 r_2} \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} X_{r_1 r_2}^2 \left(F_0 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) + 2 \frac{w_{r_1 r_2}}{X_{r_1 r_2}} F_1 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \right) \quad (41)$$

The evaluation of the SME model in the Boltzmann limit, obtained by expanding in the hard-sphere diameters and keeping only the leading order (which here amounts to taking the limit $w_{r_1 r_2} \rightarrow 0$ and using $F_0(0) = -1$ and $F_1(0) = \frac{1}{\sqrt{\pi}}$) is performed in Appendix . For a one component system, the GME results are in agreement with Chou and Richman[6],[7] while the Boltzmann limit of the SME is in agreement, for a one-component system, with the expressions given by Garzo[15]. In this simple case, the angular integrals can be performed analytically (see appendix). It is remarkable that the structure of these terms is virtually identical to the equivalent quantities which occur in the elementary case of the moment solution of the Enskog equation for USF of elastic hard spheres[13],[14]. The practical result is that it is technically no more difficult to work with an arbitrary mixture than with a single species.

Polydisperse Granular Fluids

As an extreme example, these results can be generalized to describe a polydisperse granular fluid in which there is a continuous distribution of grain sizes, masses and coefficients of restitution. This is equivalent to having an infinite

number of species and in general one must supply the distribution of grains amongst the species, i.e. x_r as well as the hard-sphere diameters, $\sigma_{r_i r_j}$ and coefficients of restitution $\alpha_{r_i r_j}$. In fact, formally, the species label can be replaced by a continuous index over some interval, say $[0, 1]$, and sums over species replaced by integrals over this index. In the event that each species has a unique hard sphere diameter σ_r , and the hard-sphere diameters are additive, i.e.

$$\sigma_{rr'} = \frac{1}{2} (\sigma_r + \sigma_{r'}) \quad (42)$$

it makes sense to replace the integrals over species labels by integrals over the distribution of hard sphere diameters. Specifically, the measures $x_r dr$ become $x_r \frac{dr}{d\sigma} d\sigma \equiv x(\sigma) d\sigma$ where $x(\sigma)$ is the fraction of grains having diameter σ . The moment equations then become

$$\begin{aligned} & n^{-1}(\sigma_1) \frac{\partial}{\partial t} n(\sigma_1) \left(\overleftrightarrow{\Gamma}(\sigma_1) \right)_{i_1 i_2}^{-1} - a \left(\delta_{i_1 x} \left(\overleftrightarrow{\Gamma}(\sigma_1) \right)_{y i_2}^{-1} + \delta_{i_2 x} \left(\overleftrightarrow{\Gamma}(\sigma_1) \right)_{y i_1}^{-1} \right) \\ &= -n \int d\sigma_2 x(\sigma_2) \chi \left(\frac{\sigma_1 + \sigma_2}{2} \right) \left(\frac{\sigma_1 + \sigma_2}{2} \right)^{D-1} (1 + \alpha(\sigma_1, \sigma_2)) \frac{\mu(\sigma_1, \sigma_2)}{m(\sigma_1)} \tilde{E}_{i_1 i_2}(\sigma_1, \sigma_2) \end{aligned} \quad (43)$$

with

$$\begin{aligned} \tilde{E}_{i_1 i_2}(\sigma_1, \sigma_2) &= - \int d\hat{q} X(\sigma_1, \sigma_2) F_1 \left(\frac{w(\sigma_1, \sigma_2)}{X(\sigma_1, \sigma_2)} \right) \left[\left(\overleftrightarrow{\Gamma}^{-1}(\sigma_1) \cdot \hat{q} \right)_{i_1} \hat{q}_{i_2} + \left(\overleftrightarrow{\Gamma}^{-1}(\sigma_1) \cdot \hat{q} \right)_{i_2} \hat{q}_{i_1} \right] \\ &\quad + \frac{1}{2} (1 + \alpha(\sigma_1, \sigma_2)) \frac{\mu(\sigma_1, \sigma_2)}{m(\sigma_1)} \\ &\quad \times \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} X^3(\sigma_1, \sigma_2) \left[\left(\frac{w(\sigma_1, \sigma_2)}{X(\sigma_1, \sigma_2)} \right) F_0 \left(\frac{w(\sigma_1, \sigma_2)}{X(\sigma_1, \sigma_2)} \right) + F_1 \left(\frac{w(\sigma_1, \sigma_2)}{X(\sigma_1, \sigma_2)} \right) \left(2 \left(\frac{w(\sigma_1, \sigma_2)}{X(\sigma_1, \sigma_2)} \right)^2 + 2 \right) \right] \\ X(\sigma_1, \sigma_2) &= \sqrt{\hat{q} \cdot \left(\overleftrightarrow{\Gamma}^{-1}(\sigma_1) + \overleftrightarrow{\Gamma}^{-1}(\sigma_2) \right) \cdot \hat{q}} \\ w(\sigma_1, \sigma_2) &= \left(\frac{\sigma_1 + \sigma_2}{2} \right) \hat{q} \cdot \overleftrightarrow{a} \cdot \hat{q} \end{aligned} \quad (44)$$

and the contributions to the pressure becomes

$$\begin{aligned} P_{i_1 i_2}^K &= n \int d\sigma_1 x(\sigma_1) \left(\overleftrightarrow{\Gamma}(\sigma_1) \right)_{i_1 i_2}^{-1} \\ P_{i_1 i_2}^V &= -\frac{1}{4} n^2 \int d\sigma_1 d\sigma_2 x(\sigma_1) x(\sigma_2) \left(\frac{\sigma_1 + \sigma_2}{2} \right)^D \chi \left(\frac{\sigma_1 + \sigma_2}{2} \right) (1 + \alpha(\sigma_1, \sigma_2)) \mu(\sigma_1, \sigma_2) \\ &\quad \times \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} X^2(\sigma_1, \sigma_2) \left(F_0 \left(\frac{w(\sigma_1, \sigma_2)}{X(\sigma_1, \sigma_2)} \right) + 2 \left(\frac{w(\sigma_1, \sigma_2)}{X(\sigma_1, \sigma_2)} \right) F_1 \left(\frac{w(\sigma_1, \sigma_2)}{X(\sigma_1, \sigma_2)} \right) \right) \end{aligned} \quad (45)$$

where some model for $\alpha(\sigma_1, \sigma_2)$ and the masses $m(\sigma_1)$ must be supplied. The generalization of the SME expressions is similarly straightforward. These expressions appear formidable to implement, but if the σ -integrals are performed using n -point Gaussian quadratures, then $\int d\sigma x(\sigma) \mathcal{F}(\sigma) \rightarrow \sum_{i=1}^n w_i x(\sigma_i) \mathcal{F}(\sigma_i)$, where w_i are the Gaussian weights and the σ_i are determined by the Gaussian abscissas. In this form, the calculation is identical to that for n -species with $x_{r_i} = w_i x(\sigma_i)$. Thus, numerically, there is no practical difference between the polydisperse fluid and a mixture with n -species.

COMPARISON TO SIMULATION

Simulation and numerical methods

In order to evaluate the models presented here, three types of calculations were performed for three dimensional systems: numerical solution of the second order moment expansions, numerical solution of the Enskog equation by means of direct simulation monte carlo (DSMC) and molecular dynamics (MD) simulations. Comparison of the first two elucidates the accuracy of the second order moment approximations while comparison of both to the MD indicates

the accuracy of the underlying assumptions: that the state obtained is indeed USF and the assumption of molecular chaos.

The focus here will be on the steady-state properties of the systems, so that when evaluating the SME and GME models, the time-derivatives are set identically to zero. Implementation of the (static) SME requires the numerical evaluation of the coefficients given in Eq.(39) and the solution of equations (28) for the partial temperatures and the shear rate as a function of the global temperature and coefficient of restitution (the second order moments are determined from Eq.(28) which are linear so that moments may be taken as given functions of the other parameters). The GME requires a similar numerical evaluation of the function $E_{ij}^{r_1 r_2}$ and solution of the nonlinear moment equations, Eqs.(25) and (27). All numerical calculations were performed using the Gnu Scientific Library[22]. In all cases, the (two dimensional) numerical integrals were calculated using the GSL routine "qags" (Gauss-Kronrod 21-point integration rule applied adaptively until the desired accuracy is achieved) with a specification of relative accuracy of 10^{-4} and absolute accuracy of 10^{-6} for the inner integral and 10^{-3} and 10^{-6} for the outer integrals. The linear equations for the SME moments were solved by LU decomposition and the nonlinear equations for the partial temperatures and shear rate were solved with the GSL "hybrids" algorithm (Powell's Hybrid method with numerical evaluation of the Jacobian). Convergence was considered to be achieved when the sum of the absolute value of the residuals was less than 10^{-7} . The same methods and tolerances were used to solve the nonlinear moment equations for the GME.

The second set of calculations performed consisted of the numerical solution of the Enskog equation by means of the Direct Simulation Monte Carlo (DSMC) method[18]. These calculations were performed using a cubic cell with sides equal to the maximum of the hard sphere diameters, with 10^5 points and a time step of $\Delta t = 0.0117\tau_{mft}$ where τ_{mft} is the mean free time. All calculations began from an initial configuration corresponding to the equilibrium hard sphere fluid. Shear flow was imposed by means of Lees-Edwards boundary conditions which are periodic boundaries in the Lagrangian frame[17]. For each combination of temperature, shear rates and coefficients of restitution, the initial configuration was relaxed over a period of $100\tau_{mft}$ and steady-state statistics, reported below, were then obtained by averaging over another $100\tau_{mft}$.

Finally, these calculations are compared below to molecular dynamics simulations. In all cases, the systems consisted of 500 grains and the starting configuration was the equilibrium fluid. Shear flow was again imposed by means of Lees-Edwards boundary conditions. After turning on the shear flow and collisional dissipation, the systems were allowed to relax for a period of 5×10^7 collisions after which statistics were gathered for another 5×10^7 collisions. Errors were computed by estimating the desired statistics using data from each period of 10^5 collisions and calculating the standard error between the estimates (the same method was used in the DSMC calculation). In the figures shown below, error bars are in general not given because in most cases, the estimated errors are comparable to or smaller than the size of the symbols. Exceptions to this (in the case of the temperature distributions) are explicitly commented upon in the text. Larger systems were not simulated as they are subject to various hydrodynamic instabilities which violate the assumption that the state is USF[23],[24].

Binary mixtures

One check on the expressions given here is to compare to the results of Montanero and Garzo who have evaluated the SME in the Boltzmann limit for a binary mixture and compared to DSMC simulations for a variety of combinations of mass, diameter and density ratios. The expressions for the SME when evaluated for $n\langle\sigma\rangle^3 = 0.001$, so as to achieve the Boltzmann limit, do indeed agree well with the data given in ref.[25]. A particular case is for $\sigma_{11} = \sigma_{12} = \sigma_{22} = 1$, $m_1 = 10m_2$, $\alpha_{11} = \alpha_{12} = \alpha_{22} = 0.75$ and $x_1 = x_2 = 0.5$ for which Montanero and Garzo report $P_{xy}^K = -0.498$ and $P_{yy}^K = 0.723$ from DSMC simulations and $P_{xy}^K = -0.498$ and $P_{yy}^K = 0.743$ from their evaluation of the SME in the Boltzmann limit. I find that the (very low density) SME gives $P_{xy}^K = -0.4981$ and $P_{yy}^K = 0.7435$ in excellent agreement. By comparison, the GME gives $P_{xy}^K = -0.496$ and $P_{yy}^K = 0.726$ and so is in even better agreement with the DSMC numerical solution of the Boltzmann equation. In addition, in the same limit, the GME is able to account for at least some of the normal stress differences, $P_{yy}^K - P_{zz}^K$, that the SME misses (in the SME in the Boltzmann limit, $P_{yy}^K = P_{zz}^K$) but which are clearly nonzero in the DSMC calculations.

Polydisperse model

A simple model was used in which the diameters are additive, the masses scale with the diameters in the usual way

$$m(\sigma) = \frac{4\pi}{3} \rho_0 \sigma^3 \quad (46)$$

and the coefficients of restitution are also additive

$$\alpha(\sigma_1, \sigma_2) = \frac{1}{2} (\alpha(\sigma_1) + \alpha(\sigma_2)). \quad (47)$$

The distribution of diameters was taken to be a simple triangular distribution

$$x(\sigma) = \begin{cases} u^{-2}(\sigma - 1 + u), & 1 - u < \sigma < 1 \\ u^{-2}(1 + u - \sigma), & 1 < \sigma < 1 + u \end{cases} \quad (48)$$

so that the average diameter is 1 and the polydispersity, defined as the variance divided by the average of the sizes, is $\delta = \frac{1}{\sqrt{6}}u$. The coefficients of restitution were assumed to scale linearly with the diameter with the smallest grains being hard, $\alpha(\sigma = 1 - u) = 1$, and the largest being soft, $\alpha(\sigma = 1 + u) = \alpha_0 < 1$, where α_0 is a free parameter, so that the average value is $\langle \alpha \rangle = \frac{1+\alpha_0}{2}$. The equilibrium pair structure function $\chi(\sigma_1, \sigma_2)$ was evaluated using the approximation of ref ([26]) and the accuracy of this approximation was verified in the equilibrium ($\alpha_0 = 1$) simulations. In all of the calculations reported here, the integrals over the distribution of hard-sphere diameters were performed using a Gauss-Legendre integration scheme with 10 points. Using 5 points, the results differed by about 10%. When evaluating the equations for an equilibrium ($\alpha_0 = 1$) mixture, the difference between the 5 and 10 point schemes was also about 10% and the absolute accuracy of the 10 point scheme compared to the known exact results was 1%. The MD and DSMC simulations were performed with a system obtained by a random sampling over the distribution of hard-sphere diameters. A variety of simulations were also performed with other samplings and it was confirmed that the results reported below do not vary significantly from sample to sample.

In the following, comparisons will be made for systems at three densities: a low density fluid, $n^* \equiv n \langle \sigma^3 \rangle = 0.1$, a moderately dense fluid $n^* = 0.25$ and a dense fluid $n^* = 0.5$. In all cases, a value of $u = 0.5$ or polydispersity of $\delta = 20.4\%$ was used. All results are from a single random sampling of this distribution. For the DSMC calculations, the large number of points used means that the distribution is well sampled. For the MD, however, the relatively small number of atoms might mean that the results reported below are influenced by the particular realization used. To control against this, I have checked a number of data points using multiple independent samplings from the distribution and confirmed that the variation induced by different samplings is negligible, at least for the properties discussed below.

Accuracy of the second moments

Figure 1 shows the kinetic part of the stress tensor, or equivalently the second moments, as obtained from the SME, the GME and the DSMC. Comparison with the numerical solution of the Enskog equation, i.e. the DSMC results, shows that the GME gives a virtually exact estimate of the second moments at all densities and degrees of inelasticity. It is interesting to note that the difference between the yy and zz moments, which is zero in the Boltzmann limit (see Appendix), is never very great and actually changes sign at high density. The SME is in close agreement with the GME. The only significant difference is in the yy and zz moments where the SME tends to underestimate the difference between them. Figure 2 compares the GME calculation to the MD results for the same systems. The calculations are in excellent agreement with the simulations at low density and remain reasonable even at the highest density. In particular, the xy moments are in good agreement at all densities. These results show that the GME gives an accurate estimate of the second velocity moments as determined by the Enskog equation and that the Enskog equation gives a reasonable approximation to the second moments at all densities investigated.

Accuracy of the second moment approximation

The next question is whether stopping at second moments is sufficient to accurately approximate the full solution of the Enskog equation. One measure of this is the calculation of the collisional contribution to the stress tensor.

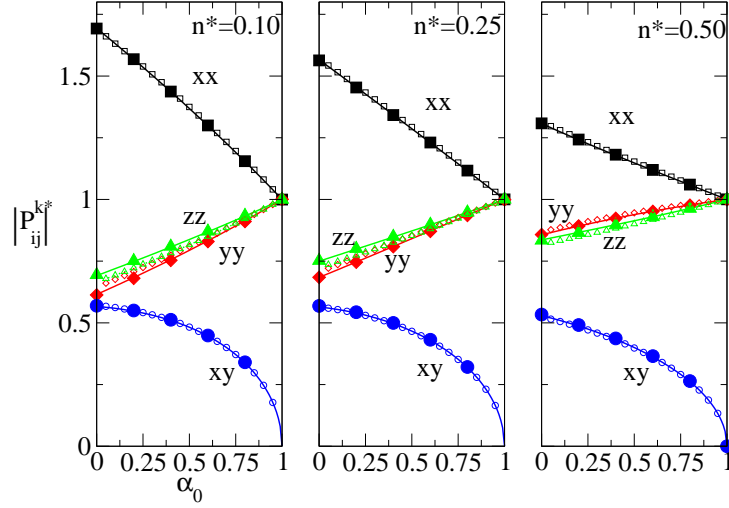


FIG. 1: The absolute values of the kinetic part of the stress tensor (i.e., the second moments) normalized to $nk_B T$ for three densities as determined by the GME (solid lines), SME (open symbols) and DSMC (filled symbols). Note that the xy moments are actually negative.

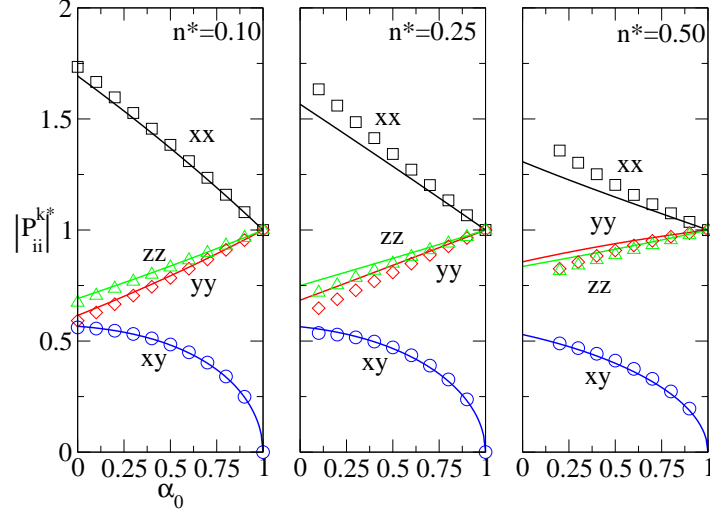


FIG. 2: Same as 1, but showing results from the GME (solid lines) and MD simulations (symbols).

Figure 3 shows the diagonal components of this quantity as calculated from the GME and DSMC and measured in the MD simulations. At low density, the agreement between the GME and DSMC is good, although not quite as good as for the moments themselves. This shows that although higher order moments will give some small contribution, the GME appears, in this case at least, to be a good approximation to the solution of the Enskog equation. However, comparison to the MD shows the shortcomings of the Enskog equation itself. At low density, agreement is good but even at moderate density, considerable differences between MD and the Enskog approximation are apparent although the latter remains a reasonable semi-quantitative approximation. At the highest density, the differences become

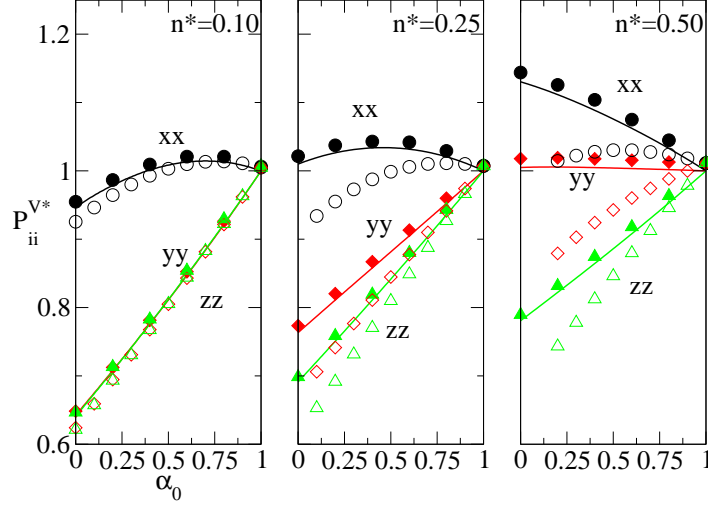


FIG. 3: The diagonal components of the collisional contribution to the stress tensor as a function of α_0 normalized to their equilibrium ($\alpha_0 = 1$) values. The lines are GME, the filled symbols DSMC and the open symbols MD.

qualitative in nature. In the MD, the xx component changes non-monotonically with α_0 whereas the Enskog theory predicts a monotonic increase with increasing inelasticity. Enskog predicts little change in the yy component whereas in fact it drops rapidly. Only the zz component is represented at all reasonably.

Viscoelastic properties

Figure 4 shows the dimensionless shear rate a^* as a function of α_0 according to the DSMC, GME and MD. All of these are in good agreement at all densities and values of inelasticity. This agreement is also fortunate since it means that any differences between Enskog and MD are not attributable to a misestimated shear rate.

Figure 5 shows the pressure (trace of the stress tensor). In contrast to elastic hard spheres, for which the pressure increases with increasing shear rate[14], the pressure is nearly constant. The calculations are again all in reasonably good agreement with the MD. Figure 6 shows the dimensionless shear viscosity

$$\eta^* = \frac{P_{xy}}{a} \sqrt{\frac{\langle \sigma \rangle^4}{k_B T \langle m \rangle}} \quad (49)$$

and the viscometric functions

$$\begin{aligned} \psi_1^* &= \frac{P_{xx} - P_{yy}}{a^2} \frac{\langle \sigma \rangle}{\langle m \rangle} \\ \psi_2^* &= \frac{P_{yy} - P_{zz}}{a^2} \frac{\langle \sigma \rangle}{\langle m \rangle} \end{aligned} \quad (50)$$

which measure the normal stresses. The Enskog theory gives a very reasonable estimate for all of the viscoelastic properties. Although ψ_1^* is systematically underestimated, ψ_2^* and the shear viscosity are well approximated at all densities. In all cases, the errors grow with density and decreasing α_0 .

Temperature distribution

So far, the comparisons have shown the Enskog theory and the MD to be in good agreement for bulk properties up to $n^* \leq 0.25$. Even above this density, the physically interesting quantities - the pressure, shear viscosity and

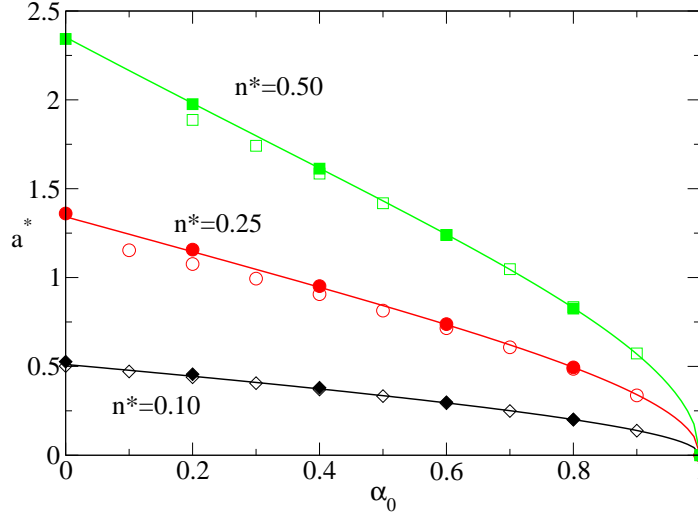


FIG. 4: The reduced shear rate a^* as a function of α_0 as determined from the GME (lines) DSMC (filled symbols) and MD (open symbols).

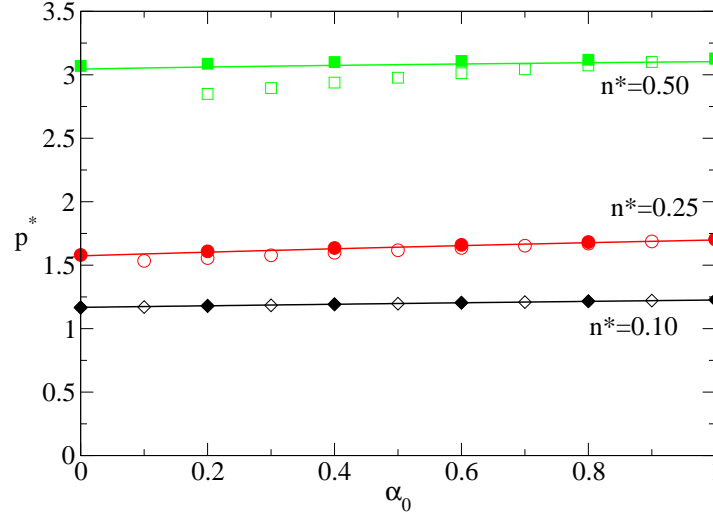


FIG. 5: Same as 5 but showing the reduced pressure $p^* = p/nk_B T$.

viscometric functions, are well approximated. This picture changes when attention focuses on variations of properties with grain species. Figure 7 shows a comparison of the predicted temperature distribution as a function of grain size according to the SME, GME and DSMC for the particular value $\alpha = 0.4$ as well as the zero density, Boltzmann limit, prediction. The SME and GME are again very good approximations to the numerical results with the former being slightly more accurate for the smaller grains and the latter more accurate for the larger grains for which the SME deviates from the Boltzmann result too slowly. The surprising result is shown in Fig. 8 which compares the distributions obtained from the GME and MD simulations. Although reasonable, the Enskog results are in poor agreement with the MD for the largest grains, especially at the *lower* densities and most especially for $n^* = 0.25$.

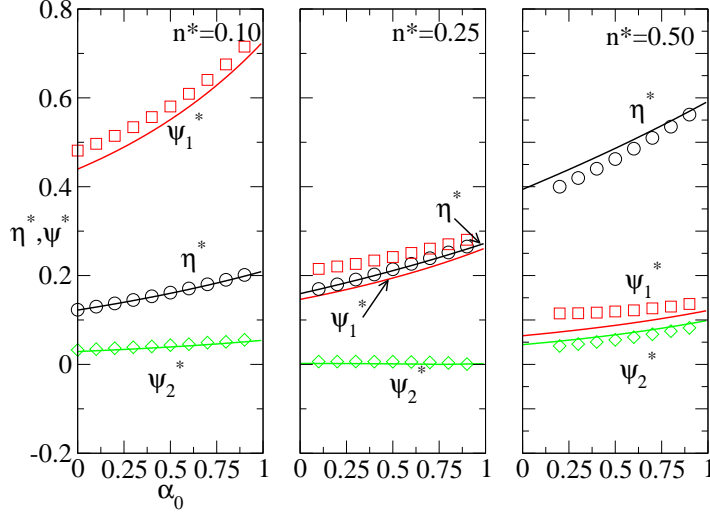


FIG. 6: The reduced shear viscosity and viscometric functions, as defined in Eqs.(49)-(50) as functions of α_0 . The lines are from the GME and the symbols from MD.

Even more surprisingly, the MD results at lower densities are in good agreement with the GME approximation to the Boltzmann equation. The two differences between the Boltzmann and Enskog theories are that (a) the Enskog theory has a higher collision frequency due to the prefactor of the pair distribution function which occurs in the collision term and (b) the Enskog theory accounts for the non-locality of the interactions of the grains in the collision term. It is hard to imagine that the second point is in error, so it seems most likely that the Enskog theory is overestimating the collision rate for large grains. Some support for this hypothesis comes from the fact that setting the pdf to its Boltzmann limit (ie. unity) increases the temperature of the largest grains by about a third of the difference between the Boltzmann and Enskog results for $n^* = 0.25$. This suggests that even at low density, the Enskog theory is based on a poor estimate of the collision rates and so that the assumption of molecular chaos, Eq.(6), is in error. This error is not apparent when considering the bulk properties because the distribution of grain sizes is such that the largest grains make a relatively small contribution to most properties: the largest contributions come from grains near the middle of the distribution where the Enskog theory is relatively accurate.

CONCLUSIONS

In this paper, the moment approximation to the solution of the Boltzmann-Enskog kinetic theory can be generalized so as to represent an expansion about an arbitrary Gaussian state. This framework encompasses both the Generalized Maxwellian approximation as well as the simple moment expansion about local equilibrium as special cases. It shows in particular how corrections to the Generalized Maxwellian approximation might be calculated.

A generating function technique was also presented as a simplified means of calculating collision integrals for the particular case of uniform shear flow. Although the present calculation were only performed to second order, the generating function technique would make higher order calculations much more feasible than more straightforward methods. The technique is based on the observation that the post-collisional velocities of hard spheres are linear functions of the pre-collisional velocities so that pre-collisional Gaussians remain Gaussian and integrals over such functions are relatively straightforward to perform. This technique is particularly valuable in anisotropic states, such as USF, where the usual approach to evaluating collision integrals becomes very messy. The method should be applicable to many other types of kinetic theory calculations.

These general methods were applied to the particular case of arbitrary mixtures of granular fluids. It was shown, by comparison to DSMC simulations, that both the SME and the GME are very good approximations to the exact solutions to the Enskog equation for a model polydisperse granular fluid. The GME tends to be slightly more accurate

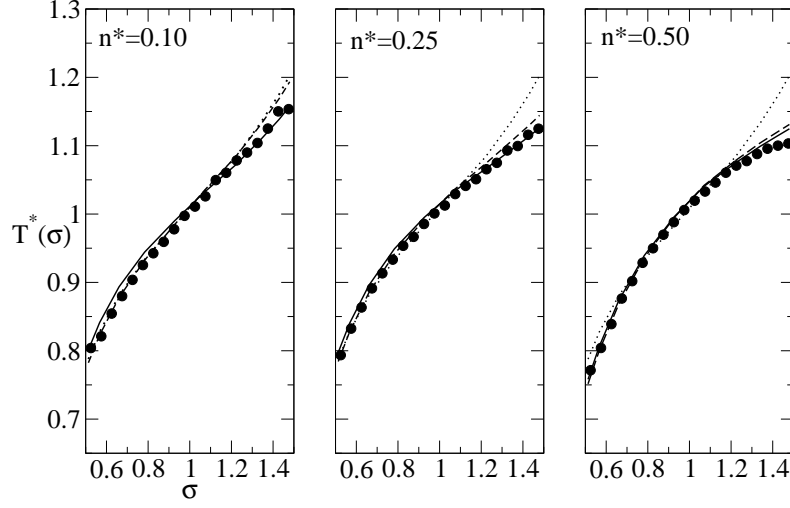


FIG. 7: The reduced temperature distribution $T^*(\sigma) = T(\sigma)/T$ as a function of grain size, σ . The line is from the GME, the filled symbols from DSMC, the dashed line is the SME and the dotted line is from the Boltzmann equation (also in the GME approximation).

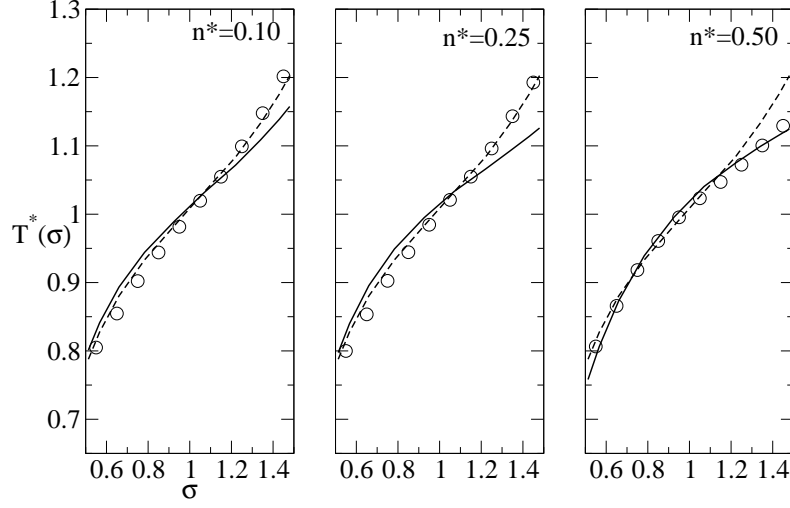


FIG. 8: The reduced temperature distribution $T^*(\sigma) = T(\sigma)/T$ as a function of grain size, σ . The full line is from the GME, the open symbols are from MD, and the dashed line is from the Boltzmann equation (also in the GME approximation).

than the SME and has the additional advantage that the approximate distribution is positive definite.

Comparison to MD simulations showed that the Enskog equation gives a good estimate of bulk properties such as the temperature, pressure, shear viscosity and viscometric functions (i.e., normal stresses) over a wide range of coefficients of restitution and densities. Shear thinning is particularly well predicted. However, a more detailed examination shows that part of this agreement (particularly in the case of the viscometric functions) is due to a cancellation of errors while the description of the variation of temperature with grain size is in fact rather poor. The

fact that this agreement is so poor even at relatively low densities raises the question of whether the approximate kinetic theory is fundamentally lacking in some way. Possible explanations of the errors are that the local equilibrium pair distribution function is simply inaccurate, that the assumption of molecular chaos is violated or that the systems are not actually in a state of USF due, e.g., to some sort of segregation process. The exploration of these possibilities will be the subject of a later work.

ACKNOWLEDGMENTS

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MOMENT EQUATIONS

In this appendix, the left hand side of the moment equations is developed, first for a general Gaussian state and then specialized to uniform shear flow. The kinetic equations take the form

$$\left(\frac{\partial}{\partial t} + \vec{v} \cdot \frac{\partial}{\partial \vec{q}} \right) f_r(\vec{q}_1, \vec{v}_1; t) = \sum_s J[f_r, f_s] \quad (51)$$

and the distribution is expanded as

$$f_r(\vec{q}, \vec{V}; \{n_s\}, T) = n_r \det(\vec{\Gamma}^r)^{1/2} \pi^{-D/2} \exp(-\vec{V}^r \cdot \vec{\Gamma}^r \cdot \vec{V}^r) \left(\sum_{n=0} \frac{1}{n!} \sum_{I_n} A_{I_n}^r H_{I_n}(\sqrt{2} \vec{\Gamma}^{r1/2} \cdot \vec{V}^r) \right) \quad (52)$$

where $\vec{V}^r = \vec{v} - \vec{u}^r(q)$. This is slightly more general than the form given in the text as we allow here for an arbitrary, species-dependent, linear contribution to the Gaussian. In the following, all dependence on space and time will not be indicated explicitly, although all quantities do in fact have such dependence. Furthermore, since we are only interested in the left hand side of the equation, which only involves a single species, the species label will also be suppressed until the end of the calculation.

The first step is to switch variables from $\{\vec{q}, \vec{v}, t\}$ to $\{\vec{q}' = \vec{q}, C_i = \sqrt{2}\Gamma_{ij}^{1/2}(v_j - u_j), t' = t\}$ using

$$\begin{aligned} \frac{\partial}{\partial t} &= \frac{\partial}{\partial t'} + \frac{\partial C_i}{\partial t} \frac{\partial}{\partial C_i} = \frac{\partial}{\partial t'} + \left(\frac{\partial \Gamma_{ij}^{1/2}}{\partial t'} \Gamma_{jl}^{-1/2} C_l - \sqrt{2} \Gamma_{ij}^{1/2} \frac{\partial u_j}{\partial t'} \right) \frac{\partial}{\partial C_i} \\ \frac{\partial}{\partial q_l} &= \frac{\partial}{\partial q'_l} + \frac{\partial C_i}{\partial q'_l} \frac{\partial}{\partial C_i} = \frac{\partial}{\partial q'_l} + \left(\frac{\partial \Gamma_{ij}^{1/2}}{\partial q'_l} \Gamma_{jk}^{-1/2} C_k - \sqrt{2} \Gamma_{ij}^{1/2} \frac{\partial u_j}{\partial q'_l} \right) \frac{\partial}{\partial C_i} \end{aligned} \quad (53)$$

so that

$$\begin{aligned} \frac{\partial}{\partial t} + \vec{v} \cdot \frac{\partial}{\partial \vec{q}} &= \frac{\partial}{\partial t'} + \left(\frac{\partial \Gamma_{ij}^{1/2}}{\partial t} \Gamma_{jk}^{-1/2} C_k - \sqrt{2} \Gamma_{ij}^{1/2} \frac{\partial u_j}{\partial t} \right) \frac{\partial}{\partial C_i} \\ &+ \left(\frac{1}{\sqrt{2}} \Gamma_{lm}^{-1/2} C_m + u_l \right) \left(\frac{\partial}{\partial q'_l} + \left(\frac{\partial \Gamma_{ij}^{1/2}}{\partial q'_l} \Gamma_{jk}^{-1/2} C_k - \sqrt{2} \Gamma_{ij}^{1/2} \frac{\partial u_j}{\partial q'_l} \right) \frac{\partial}{\partial C_i} \right). \end{aligned} \quad (54)$$

Introducing $\tilde{f} = \det \left(2 \overleftrightarrow{\Gamma} \right)^{-1/2} f$, the kinetic equation becomes

$$\begin{aligned}
& \frac{\partial}{\partial t'} \tilde{f} + \left(\frac{\partial \Gamma_{ij}^{1/2}}{\partial t} \Gamma_{jk}^{-1/2} C_k - \sqrt{2} \Gamma_{ij}^{1/2} \frac{\partial u_j}{\partial t} \right) \frac{\partial}{\partial C_i} \tilde{f} \\
& + \left(\frac{1}{\sqrt{2}} \Gamma_{lm}^{-1/2} C_m + u_l \right) \left(\frac{\partial}{\partial q'_l} + \left(\frac{\partial \Gamma_{ij}^{1/2}}{\partial q'_l} \Gamma_{jk}^{-1/2} C_k - \sqrt{2} \Gamma_{ij}^{1/2} \frac{\partial u_j}{\partial q'_l} \right) \frac{\partial}{\partial C_i} \right) \tilde{f} \\
& + \frac{\partial}{\partial t'} \ln \det \left(\overleftrightarrow{\Gamma} \right)^{1/2} + \left(\frac{1}{\sqrt{2}} \Gamma_{lm}^{-1/2} C_m + u_l \right) \frac{\partial}{\partial q'_l} \ln \det \left(\overleftrightarrow{\Gamma} \right)^{1/2} \\
& = \det \left(2 \overleftrightarrow{\Gamma}^r \right)^{-1/2} \sum_s J[f_r, f_s].
\end{aligned} \tag{55}$$

The next step is to multiply through by $H_{I_n} \left(\overrightarrow{C} \right)$ and to integrate over \overrightarrow{C} . These evaluations are performed using the basic identities, which follow directly from the definition of the Hermite polynomials,

$$\begin{aligned}
C_x H_{I_n} \left(\overrightarrow{C} \right) &= H_{x I_n} \left(\overrightarrow{C} \right) + \mathcal{S}_{I_n} \delta_{i_n x} H_{I_{n-1}} \left(\overrightarrow{C} \right) \\
\frac{\partial}{\partial C_x} H_{I_n} \left(\overrightarrow{C} \right) &= \mathcal{S}_{I_n} \delta_{i_n x} H_{I_{n-1}} \left(\overrightarrow{C} \right)
\end{aligned} \tag{56}$$

where the operator \mathcal{S}_{I_n} indicates a sum over all inequivalent permutations of the indicated set of indices. Repeated application of these gives

$$\begin{aligned}
C_x C_y H_{I_n} \left(\overrightarrow{C} \right) &= H_{I_n xy} \left(\overrightarrow{C} \right) + \delta_{xy} H_{I_n} \left(\overrightarrow{C} \right) \\
&+ \mathcal{S}_{I_n} \left(\delta_{x i_n} \delta_{y i_{n-1}} H_{I_{n-2}} \left(\overrightarrow{C} \right) + \delta_{x i_n} H_{I_{n-1} y} \left(\overrightarrow{C} \right) + \delta_{y i_n} H_{I_{n-1} x} \left(\overrightarrow{C} \right) \right) \\
C_y \frac{\partial}{\partial C_x} H_{I_n} \left(\overrightarrow{C} \right) &= \mathcal{S}_{I_n} \delta_{i_n x} H_{y I_{n-1}} \left(\overrightarrow{C} \right) + \mathcal{S}_{I_n} \delta_{i_n x} \delta_{i_{n-1} y} H_{I_{n-2}} \left(\overrightarrow{C} \right) \\
C_z C_y \frac{\partial}{\partial C_x} H_{I_n} \left(\overrightarrow{C} \right) &= \mathcal{S}_{I_n} \delta_{i_n x} \left(H_{I_{n-1} zy} \left(\overrightarrow{C} \right) + \delta_{zy} H_{I_{n-1}} \left(\overrightarrow{C} \right) + \delta_{z i_{n-1}} \delta_{y i_{n-2}} H_{I_{n-3}} \left(\overrightarrow{C} \right) \right. \\
&\quad \left. + \delta_{z i_{n-1}} H_{I_{n-2} y} \left(\overrightarrow{C} \right) + \delta_{y i_{n-1}} H_{I_{n-2} z} \left(\overrightarrow{C} \right) \right).
\end{aligned} \tag{57}$$

Combined with the orthonormality of the Hermite polynomials, and integrating by parts where needed, one then has that

$$\begin{aligned}
n^{-1} \int d\overrightarrow{C} H_{I_n} \left(\overrightarrow{C} \right) \tilde{f} \left(\overrightarrow{C} \right) &= A_{I_n} \\
n^{-1} \int d\overrightarrow{C} C_x H_{I_n} \left(\overrightarrow{C} \right) \tilde{f} \left(\overrightarrow{C} \right) &= A_{x I_n} + \mathcal{S}_{I_n} \delta_{i_n x} A_{I_{n-1}} \\
n^{-1} \int d\overrightarrow{C} C_y H_{I_n} \left(\overrightarrow{C} \right) \frac{\partial}{\partial C_x} \tilde{f} \left(\overrightarrow{C} \right) &= -\delta_{xy} A_{I_n} - \mathcal{S}_{I_n} \delta_{i_n x} \left(A_{y I_{n-1}} + \delta_{i_{n-1} y} A_{I_{n-2}} \right) \\
n^{-1} \int d\overrightarrow{C} C_z C_y H_{I_n} \left(\overrightarrow{C} \right) \frac{\partial}{\partial C_x} \tilde{f} \left(\overrightarrow{C} \right) &= -\mathcal{S}_{yz} \delta_{xy} \left(A_{z I_n} + \mathcal{S}_{I_n} \delta_{i_n z} A_{I_{n-1}} \right) \\
&\quad - \mathcal{S}_{I_n} \delta_{i_n x} \left(H_{I_{n-1} zy} \left(\overrightarrow{C} \right) + \delta_{zy} H_{I_{n-1}} \left(\overrightarrow{C} \right) \right) \\
&\quad - \mathcal{S}_{I_n} \delta_{i_n x} \left(H_{\delta_{z i_{n-1}} \delta_{y i_{n-2}} H_{I_{n-3}} \left(\overrightarrow{C} \right) + \mathcal{S}_{yz} \delta_{z i_{n-1}} H_{I_{n-2} y} \left(\overrightarrow{C} \right) \right).
\end{aligned} \tag{58}$$

Using these, the kinetic equation becomes

$$\begin{aligned}
& n_r^{-1} \frac{\partial}{\partial t'} n_r A_{I_n}^r + n_r^{-1} \frac{\partial}{\partial q_l^r} n_r u_l^r A_{I_n}^r - \mathcal{S}_{I_n} \left(\frac{\partial \Gamma_{in,j}^{r1/2}}{\partial t} \Gamma_{jk}^{r-1/2} + u_l^r \frac{\partial \Gamma_{in,j}^{r1/2}}{\partial q_l^r} \Gamma_{jk}^{r-1/2} - \Gamma_{in,j}^{r1/2} \frac{\partial u_j^r}{\partial q_l^r} \Gamma_{lk}^{r-1/2} \right) (A_{kI_{n-1}}^r + \delta_{ki_{n-1}} A_{I_n}^r) \\
& + \sqrt{2} \mathcal{S}_{I_n} \Gamma_{in,j}^{r1/2} \left(\left(\frac{\partial u_j^r}{\partial t} + u_l^r \frac{\partial u_j^r}{\partial q_l^r} \right) A_{I_{n-1}}^r + \frac{1}{2} \frac{\partial}{\partial q_l^r} (\Gamma_{jl}^{r-1} A_{I_{n-1}}^r) \right) \\
& - \frac{1}{\sqrt{2}} \mathcal{S}_{I_n} \left(\frac{\partial \Gamma_{in,j}^{r1/2}}{\partial q_l^r} \Gamma_{ji_{n-2}}^{r-1/2} \Gamma_{li_{n-1}}^{r-1/2} \right) A_{I_{n-3}}^r \\
& + n_r^{-1} \frac{1}{\sqrt{2}} \frac{\partial}{\partial q_l^r} (\Gamma_{lm}^{r-1/2} n_r A_{mI_n}^r) - \frac{1}{\sqrt{2}} \mathcal{S}_{I_n} \left(\left(\frac{\partial \Gamma_{in,j}^{r1/2}}{\partial q_l^r} \Gamma_{jk}^{r-1/2} \right) \Gamma_{lm}^{r-1/2} A_{I_{n-1}mk}^r \right) \\
& - \frac{1}{\sqrt{2}} \mathcal{S}_{I_n} \left(\left(\frac{\partial \Gamma_{in,j}^{r1/2}}{\partial q_l^r} \Gamma_{jk}^{r-1/2} \right) \Gamma_{li_{n-1}}^{r-1/2} + \left(\frac{\partial \Gamma_{in,j}^{r1/2}}{\partial q_l^r} \Gamma_{ji_{n-1}}^{r-1/2} \right) \Gamma_{lk}^{r-1/2} \right) A_{I_{n-2}k}^r \\
& = n_r^{-1} \det \left(\overleftrightarrow{\Gamma}^r \right)^{-1/2} \int d\vec{C}^r H_{I_n} \left(\vec{C}^r \right) \sum_s J[f_r, f_s].
\end{aligned} \tag{59}$$

The zeroth order equation gives

$$n_r^{-1} \frac{\partial}{\partial t'} n_r + n_r^{-1} \frac{\partial}{\partial q_l^r} n_r u_l^r = 0$$

so that the general equation becomes

$$\begin{aligned}
& \frac{\partial}{\partial t'} A_{I_n}^r + u_l^r \frac{\partial}{\partial q_l^r} A_{I_n}^r - \mathcal{S}_{I_n} \left(\frac{\partial \Gamma_{in,j}^{r1/2}}{\partial t} \Gamma_{jk}^{r-1/2} + u_l^r \frac{\partial \Gamma_{in,j}^{r1/2}}{\partial q_l^r} \Gamma_{jk}^{r-1/2} - \Gamma_{in,j}^{r1/2} \frac{\partial u_j^r}{\partial q_l^r} \Gamma_{lk}^{r-1/2} \right) (A_{kI_{n-1}}^r + \delta_{ki_{n-1}} A_{I_{n-2}}^r) \\
& + \sqrt{2} \mathcal{S}_{I_n} \Gamma_{in,j}^{r1/2} \left(\left(\frac{\partial u_j^r}{\partial t} + u_l^r \frac{\partial u_j^r}{\partial q_l^r} \right) A_{I_{n-1}}^r + \frac{1}{2} n_r^{-1} \frac{\partial}{\partial q_l^r} (n_r \Gamma_{jl}^{r-1} A_{I_{n-1}}^r) \right) \\
& - \frac{1}{\sqrt{2}} \mathcal{S}_{I_n} \left(\frac{\partial \Gamma_{in,j}^{r1/2}}{\partial q_l^r} \Gamma_{ji_{n-2}}^{r-1/2} \Gamma_{li_{n-1}}^{r-1/2} \right) A_{I_{n-3}}^r \\
& + n_r^{-1} \frac{1}{\sqrt{2}} \frac{\partial}{\partial q_l^r} (\Gamma_{lm}^{r-1/2} n_r A_{mI_n}^r) - \frac{1}{\sqrt{2}} \mathcal{S}_{I_n} \left(\left(\frac{\partial \Gamma_{in,j}^{r1/2}}{\partial q_l^r} \Gamma_{jk}^{r-1/2} \right) \Gamma_{lm}^{r-1/2} A_{I_{n-1}mk}^r \right) \\
& - \frac{1}{\sqrt{2}} \mathcal{S}_{I_n} \left(\left(\frac{\partial \Gamma_{in,j}^{r1/2}}{\partial q_l^r} \Gamma_{jk}^{r-1/2} \right) \Gamma_{li_{n-1}}^{r-1/2} + \left(\frac{\partial \Gamma_{in,j}^{r1/2}}{\partial q_l^r} \Gamma_{ji_{n-1}}^{r-1/2} \right) \Gamma_{lk}^{r-1/2} \right) A_{I_{n-2}k}^r \\
& = n_r^{-1} \det \left(\overleftrightarrow{\Gamma}^r \right)^{-1/2} \int d\vec{C}^r H_{I_n} \left(\vec{C}^r \right) \sum_s J[f_r, f_s].
\end{aligned} \tag{60}$$

Specializing to USF gives

$$\begin{aligned}
& \frac{\partial}{\partial t'} A_{I_n}^r - \mathcal{S}_{I_n} \left(\frac{\partial \Gamma_{in,j}^{r1/2}}{\partial t} \Gamma_{jk}^{r-1/2} - a_{jl} \Gamma_{in,j}^{r1/2} \Gamma_{lk}^{r-1/2} \right) (A_{kI_{n-1}}^r + \delta_{ki_{n-1}} A_{I_{n-2}}^r) \\
& = n_r^{-1} \det \left(2 \overleftrightarrow{\Gamma}^r \right)^{-1/2} \int d\vec{C}^r H_{I_n} \left(\vec{C}^r \right) \sum_s J[f_r, f_s] \\
& = n_r^{-1} \int d\vec{V}^r H_{I_n} \left(\vec{C}^r \right) \sum_s J[f_r, f_s]
\end{aligned} \tag{61}$$

For the second order GME, this gives

$$-\frac{\partial \Gamma_{i_2j}^{r1/2}}{\partial t} \Gamma_{ji_1}^{r-1/2} - \frac{\partial \Gamma_{i_1j}^{r1/2}}{\partial t} \Gamma_{ji_2}^{r-1/2} + a_{jl} \Gamma_{i_2j}^{r1/2} \Gamma_{li_1}^{r-1/2} + a_{jl} \Gamma_{i_1j}^{r1/2} \Gamma_{li_2}^{r-1/2} = n_r^{-1} \cdot \int d\vec{V}^r H_{I_n} \left(\vec{C}^r \right) \sum_s J[f_r, f_s] \tag{62}$$

Multiplying through by $\Gamma_{k_2 i_2}^{r-1/2} \Gamma_{k_1 i_1}^{r-1/2}$ and summing over i_1 and i_2 gives

$$\begin{aligned} \frac{\partial \Gamma_{k_1 k_2}^{r-1}}{\partial t} + a_{k_2 l} \Gamma_{k_1 l}^{r-1} + a_{k_1 l} \Gamma_{k_2 l}^{r-1} &= n_r^{-1} \int d\vec{V}^r \sum_{I_2} \Gamma_{k_2 i_2}^{r-1/2} \Gamma_{k_1 i_1}^{r-1/2} H_{I_2}(\vec{C}^r) \sum_s J[f_r, f_s] \\ &= 2n_r^{-1} \int d\vec{V}^r V_{k_1} V_{k_2} \sum_s J[f_r, f_s]. \end{aligned} \quad (63)$$

For the second order SME, one has

$$\frac{\partial}{\partial t'} A_{I_2}^r + \frac{\partial \ln T_r}{\partial t} A_{i_1 i_2}^r + a_{i_2 k} A_{k i_1}^r + a_{i_1 k} A_{k i_2}^r + \frac{\partial \ln T_r}{\partial t} \delta_{i_2 i_1} + a_{i_2 i_1} + a_{i_1 i_2} = n_r^{-1} \frac{m_r}{k_B T_r} \int d\vec{V}^r V_{k_1} V_{k_2} \sum_s J[f_r, f_s]$$

THE GENERATING FUNCTION

To evaluate the various kinetic integrals, we need the generating function

$$\begin{aligned} Z_{[n]}^{r_1 r_2} &= -\pi^{-D} \int d\vec{V}_1 d\vec{V}_2 d\vec{q}_2 \left(\prod_{j=1}^n \vec{q}_{12i} \right) \exp(\vec{\Lambda} \cdot \vec{V}_1) \bar{T}_-(12) \exp(-\vec{V}_1 \cdot \overleftarrow{\Gamma}^{r_1} \cdot \vec{V}_1 - \vec{V}_2 \cdot \overleftarrow{\Gamma}^{r_2} \cdot \vec{V}_2) \\ &= \pi^{-D} \int d\vec{V}_1 d\vec{V}_2 d\vec{q}_2 \left(\prod_{j=1}^n \vec{q}_{12i} \right) \exp(-\vec{V}_1 \cdot \overleftarrow{\Gamma}^{r_1} \cdot \vec{V}_1 - \vec{V}_2 \cdot \overleftarrow{\Gamma}^{r_2} \cdot \vec{V}_2) T_+(12) \exp(\vec{\Lambda} \cdot \vec{V}_1) \end{aligned} \quad (64)$$

where the negative adjoint of the collision operator is

$$T_+(12) = -\delta(q_{12} - \sigma_{r_1 r_2}) \Theta(-\vec{v}_{12} \cdot \hat{q}_{12}) \vec{v}_{12} \cdot \hat{q}_{12} [\hat{b}_{12} - 1] \quad (65)$$

and in this appendix, I continue the generalization of the first appendix and allow for an arbitrary flow state so that $\vec{V}_i = \vec{v}_i - \vec{u}^{r_i}(\vec{q}_i)$. Using

$$\hat{b}_{12} \vec{V}_1 = \vec{V}_1 - (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} (\vec{v}_{12} \cdot \hat{q}_{12}) \hat{q}_{12} \quad (66)$$

the generating function is

$$\begin{aligned} Z_{[n]}^{r_1 r_2} &= -\pi^{-D} \sigma_{r_1 r_2}^{D-1} \int d\vec{V}_1 d\vec{V}_2 d\hat{q} \left(\prod_{j=1}^n \sigma_{r_1 r_2} \hat{q}_i \right) \exp(-\vec{V}_1 \cdot \overleftarrow{\Gamma}^{r_1} \cdot \vec{V}_1 - \vec{V}_2 \cdot \overleftarrow{\Gamma}^{r_2} \cdot \vec{V}_1) \\ &\times \Theta(-\vec{v}_{12} \cdot \hat{q}) (\vec{v}_{12} \cdot \hat{q}) \left(\exp(\vec{\Lambda} \cdot \vec{V}_1 - (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} (\vec{v}_{12} \cdot \hat{q}) \vec{\Lambda} \cdot \hat{q}_{12}) - \exp(\vec{\Lambda} \cdot \vec{V}_1) \right). \end{aligned} \quad (67)$$

It is enough to restrict attention to the function

$$\begin{aligned} \tilde{Z}^{r_1 r_2}(x) &= -2 \det(\overleftarrow{\Gamma}^{r_1} \overleftarrow{\Gamma}^{r_2})^{1/2} \pi^{-D} \int d\vec{V}_1 d\vec{V}_2 \Theta(-\vec{v}_{12} \cdot \hat{q}) (\vec{v}_{12} \cdot \hat{q}) \exp(-g_{12}) \\ g_{12} &= -\vec{V}_1 \cdot \overleftarrow{\Gamma}^{r_1} \cdot \vec{V}_1 - \vec{V}_2 \cdot \overleftarrow{\Gamma}^{r_2} \cdot \vec{V}_2 + \vec{\Lambda} \cdot \vec{V}_1 - x (\vec{v}_{12} \cdot \hat{q}) \vec{\Lambda} \cdot \hat{q}_{12}. \end{aligned} \quad (68)$$

in terms of which the full generating function is

$$Z_{[n]}^{r_1 r_2} = \frac{1}{2} \sigma_{r_1 r_2}^{D-1} \det(\overleftarrow{\Gamma}^{r_1} \overleftarrow{\Gamma}^{r_2})^{-1/2} \int d\hat{q} \left(\prod_{j=1}^n \sigma_{r_1 r_2} \hat{q}_i \right) \left(\tilde{Z}^{rs} \left((1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} \right) - \tilde{Z}^{rs}(0) \right) \quad (69)$$

The velocity integrals are performed by switching to relative and center of mass (CM) coordinates

$$\begin{aligned}\vec{v} &= \vec{V}_1 - \vec{V}_2 \\ \vec{V} &= \frac{m_{r_1}}{m_{r_1} + m_{r_2}} \vec{V}_1 + \frac{m_{r_2}}{m_{r_1} + m_{r_2}} \vec{V}_2\end{aligned}\tag{70}$$

so that

$$\begin{aligned}\vec{V}_1 &= \vec{V} + \frac{\mu_{r_1 r_2}}{m_{r_1}} \vec{v} \\ \vec{V}_2 &= \vec{V} - \frac{\mu_{r_1 r_2}}{m_{r_2}} \vec{v}.\end{aligned}\tag{71}$$

In terms of the CM variables, the argument of the exponential is expanded by first using

$$\begin{aligned}-\vec{V}_1 \cdot \overleftarrow{\Gamma}^{r_1} \cdot \vec{V}_1 - \vec{V}_2 \cdot \overleftarrow{\Gamma}^{r_2} \cdot \vec{V}_2 &= -\vec{V} \cdot (\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}) \cdot \vec{V} - \vec{v} \cdot \left(\left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \right)^2 \overleftarrow{\Gamma}^{r_1} - \left(\frac{\mu_{r_1 r_2}}{m_{r_2}} \right)^2 \overleftarrow{\Gamma}^{r_2} \right) \cdot \vec{v} \\ &\quad - 2\vec{V} \cdot \left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \overleftarrow{\Gamma}^{r_1} - \frac{\mu_{r_1 r_2}}{m_{r_2}} \overleftarrow{\Gamma}^{r_2} \right) \cdot \vec{v}\end{aligned}\tag{72}$$

and the remaining terms become

$$\begin{aligned}\vec{\Lambda} \cdot \vec{V}_1 - x (\vec{v}_{12} \cdot \hat{q}_{12}) \vec{\Lambda} \cdot \hat{q} \\ = \vec{\Lambda} \cdot \vec{V} + \frac{\mu_{r_1 r_2}}{m_{r_1}} \vec{\Lambda} \cdot \vec{v} - x (\vec{\Lambda} \cdot \hat{q}) \vec{v} \cdot \hat{q} - x w_{r_1 r_2} \vec{\Lambda} \cdot \hat{q}\end{aligned}\tag{73}$$

where $w_{r_1 r_2} \equiv (\vec{u}^{r_1}(\vec{q}_1) - \vec{u}^{r_2}(\vec{q}_1 - \sigma_{r_1 r_2} \hat{q})) \cdot \hat{q}$ (in USF, $w_{r_1 r_2} = \sigma_{r_1 r_2} \hat{q} \cdot \overleftarrow{a} \cdot \hat{q}$). The first step is to complete the square in \vec{V}

$$\begin{aligned}-\vec{V} \cdot (\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}) \cdot \vec{V} - 2\vec{V} \cdot \left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \overleftarrow{\Gamma}^{r_1} - \frac{\mu_{r_1 r_2}}{m_{r_2}} \overleftarrow{\Gamma}^{r_2} \right) \cdot \vec{v} + \vec{\Lambda} \cdot \vec{V} \\ = -(\vec{V} + \vec{A}) \cdot (\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}) \cdot (\vec{V} + \vec{A}) + \vec{A} \cdot (\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}) \cdot \vec{A}\end{aligned}\tag{74}$$

with

$$\vec{A} = \vec{v} \cdot \left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \overleftarrow{\Gamma}^{r_1} - \frac{\mu_{r_1 r_2}}{m_{r_2}} \overleftarrow{\Gamma}^{r_2} \right) \cdot (\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2})^{-1} - \frac{1}{2} \vec{\Lambda} \cdot (\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2})^{-1}.\tag{75}$$

giving

$$\begin{aligned}g_{12} &= -(\vec{V} + \vec{A}) \cdot (\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}) \cdot (\vec{V} + \vec{A}) + \vec{A} \cdot (\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}) \cdot \vec{A} \\ &\quad - \vec{v} \cdot \left(\left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \right)^2 \overleftarrow{\Gamma}^{r_1} - \left(\frac{\mu_{r_1 r_2}}{m_{r_2}} \right)^2 \overleftarrow{\Gamma}^{r_2} \right) \cdot \vec{v} \\ &\quad + \frac{\mu_{r_1 r_2}}{m_{r_1}} \vec{\Lambda} \cdot \vec{v} - x (\vec{\Lambda} \cdot \hat{q}) \vec{v} \cdot \hat{q} - x w_{r_1 r_2} \vec{\Lambda} \cdot \hat{q}\end{aligned}\tag{76}$$

This can be simplified by expanding the second term and using

$$\begin{aligned}&\left(\left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \overleftarrow{\Gamma}^{r_1} - \frac{\mu_{r_1 r_2}}{m_{r_2}} \overleftarrow{\Gamma}^{r_2} \right) \cdot \vec{v} \right) \cdot (\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2})^{-1} \cdot \left(\left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \overleftarrow{\Gamma}^{r_1} - \frac{\mu_{r_1 r_2}}{m_{r_2}} \overleftarrow{\Gamma}^{r_2} \right) \cdot \vec{v} \right) \\ &- \vec{v} \cdot \left(\left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \right)^2 \overleftarrow{\Gamma}^{r_1} - \left(\frac{\mu_{r_1 r_2}}{m_{r_2}} \right)^2 \overleftarrow{\Gamma}^{r_2} \right) \cdot \vec{v} \\ &= -\vec{v} \cdot \overleftarrow{\Gamma}^{r_2} \cdot (\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2})^{-1} \cdot \overleftarrow{\Gamma}^{r_1} \cdot \vec{v}\end{aligned}\tag{77}$$

so that

$$\begin{aligned}
g_{12} = & -\left(\vec{V} + \vec{A}\right) \cdot \left(\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}\right) \cdot \left(\vec{V} + \vec{A}\right) \\
& - \vec{v} \cdot \overleftarrow{\Gamma}^{r_2} \cdot \left(\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}\right)^{-1} \cdot \overleftarrow{\Gamma}^{r_1} \cdot \vec{v} \\
& - \vec{\Lambda} \cdot \left(\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}\right)^{-1} \cdot \left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \overleftarrow{\Gamma}^{r_1} - \frac{\mu_{r_1 r_2}}{m_{r_2}} \overleftarrow{\Gamma}^{r_2}\right) \cdot \vec{v} \\
& + \frac{1}{4} \vec{\Lambda} \cdot \left(\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}\right)^{-1} \cdot \vec{\Lambda} \\
& + \frac{\mu_{r_1 r_2}}{m_{r_1}} \vec{\Lambda} \cdot \vec{v} - x \left(\vec{\Lambda} \cdot \hat{q}\right) \vec{v} \cdot \hat{q} - x w_{r_1 r_2} \vec{\Lambda} \cdot \hat{q}.
\end{aligned} \tag{78}$$

Furthermore,

$$\begin{aligned}
& \vec{\Lambda} \cdot \left(\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}\right)^{-1} \cdot \left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \overleftarrow{\Gamma}^{r_1} - \frac{\mu_{r_1 r_2}}{m_{r_2}} \overleftarrow{\Gamma}^{r_2}\right) \cdot \vec{v} \\
= & \left(\frac{\mu_{r_1 r_2}}{m_{r_1}}\right) \vec{\Lambda} \cdot \vec{v} - \vec{\Lambda} \cdot \left(\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}\right)^{-1} \cdot \overleftarrow{\Gamma}^{r_2} \cdot \vec{v}
\end{aligned} \tag{79}$$

so

$$\begin{aligned}
g_{12} = & -\left(\vec{V} + \vec{A}\right) \cdot \left(\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}\right) \cdot \left(\vec{V} + \vec{A}\right) \\
& - \vec{v} \cdot \overleftarrow{\Gamma}^{r_2} \cdot \left(\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}\right)^{-1} \cdot \overleftarrow{\Gamma}^{r_1} \cdot \vec{v} \\
& + \vec{\Lambda} \cdot \left(\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}\right)^{-1} \cdot \overleftarrow{\Gamma}^{r_2} \cdot \vec{v} \\
& + \frac{1}{4} \vec{\Lambda} \cdot \left(\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}\right)^{-1} \cdot \vec{\Lambda} \\
& - x \left(\vec{\Lambda} \cdot \hat{q}\right) \vec{v} \cdot \hat{q} - x w_{r_1 r_2} \vec{\Lambda} \cdot \hat{q}.
\end{aligned} \tag{80}$$

Next, we complete the square in \vec{v} using

$$\begin{aligned}
& - \vec{v} \cdot \overleftarrow{\Gamma}^{r_2} \cdot \left(\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}\right)^{-1} \cdot \overleftarrow{\Gamma}^{r_1} \cdot \vec{v} + \vec{\Lambda} \cdot \left(\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}\right)^{-1} \cdot \overleftarrow{\Gamma}^{r_2} \cdot \vec{v} - x \left(\vec{\Lambda} \cdot \hat{q}\right) \vec{v} \cdot \hat{q} \\
= & - \vec{v} \cdot \left(\overleftarrow{\Gamma}^{r_1-1} + \overleftarrow{\Gamma}^{r_2-1}\right)^{-1} \cdot \vec{v} + \left(\vec{\Lambda} \cdot \left(\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}\right)^{-1} \cdot \overleftarrow{\Gamma}^{r_2} - x \left(\vec{\Lambda} \cdot \hat{q}\right) \hat{q}\right) \cdot \vec{v} \\
= & - \left(\vec{v} + \vec{B}\right) \cdot \left(\overleftarrow{\Gamma}^{r_1-1} + \overleftarrow{\Gamma}^{r_2-1}\right)^{-1} \cdot \left(\vec{v} + \vec{B}\right) + \vec{B} \cdot \left(\overleftarrow{\Gamma}^{r_1-1} + \overleftarrow{\Gamma}^{r_2-1}\right)^{-1} \cdot \vec{B}
\end{aligned} \tag{81}$$

where

$$\begin{aligned}
\vec{B} = & -\frac{1}{2} \vec{\Lambda} \cdot \left(\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}\right)^{-1} \cdot \overleftarrow{\Gamma}^{r_2} \cdot \left(\overleftarrow{\Gamma}^{r_1-1} + \overleftarrow{\Gamma}^{r_2-1}\right) + \frac{1}{2} x \left(\vec{\Lambda} \cdot \hat{q}\right) \hat{q} \cdot \left(\overleftarrow{\Gamma}^{r_1-1} + \overleftarrow{\Gamma}^{r_2-1}\right) \\
= & -\frac{1}{2} \vec{\Lambda} \cdot \overleftarrow{\Gamma}^{r_1-1} + \frac{1}{2} x \left(\vec{\Lambda} \cdot \hat{q}\right) \hat{q} \cdot \left(\overleftarrow{\Gamma}^{r_1-1} + \overleftarrow{\Gamma}^{r_2-1}\right)
\end{aligned} \tag{82}$$

giving

$$\begin{aligned}
g_{12} = & -\left(\vec{V} + \vec{A}\right) \cdot \left(\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}\right) \cdot \left(\vec{V} + \vec{A}\right) \\
& - \left(\vec{v} + \vec{B}\right) \cdot \left(\overleftarrow{\Gamma}^{r_1-1} + \overleftarrow{\Gamma}^{r_2-1}\right)^{-1} \cdot \left(\vec{v} + \vec{B}\right) \\
& + \vec{B} \cdot \left(\overleftarrow{\Gamma}^{r_1-1} + \overleftarrow{\Gamma}^{r_2-1}\right)^{-1} \cdot \vec{B} \\
& + \frac{1}{4} \vec{\Lambda} \cdot \left(\overleftarrow{\Gamma}^{r_1} + \overleftarrow{\Gamma}^{r_2}\right)^{-1} \cdot \vec{\Lambda} \\
& - x w_{r_1 r_2} \vec{\Lambda} \cdot \hat{q}.
\end{aligned} \tag{83}$$

Then, using

$$\begin{aligned} \int \exp \left(- \left(\vec{V} + \vec{A} \right) \cdot \left(\overleftrightarrow{\Gamma}^{r_1} + \overleftrightarrow{\Gamma}^{r_2} \right) \cdot \left(\vec{V} + \vec{A} \right) \right) d\vec{V} &= \det \left(\overleftrightarrow{\Gamma}^{r_1} + \overleftrightarrow{\Gamma}^{r_2} \right)^{-1/2} \int \exp \left(-V^2 \right) d\vec{V} \\ &= \pi^{D/2} \det \left(\overleftrightarrow{\Gamma}^{r_1} + \overleftrightarrow{\Gamma}^{r_2} \right)^{-1/2} \end{aligned} \quad (84)$$

gives

$$\begin{aligned} \tilde{Z}^{r_1 r_2}(x) &= -2 \det \left(\overleftrightarrow{\Gamma}^{r_1} \overleftrightarrow{\Gamma}^{r_2} \right)^{1/2} \pi^{D/2} \det \left(\overleftrightarrow{\Gamma}^{r_1} + \overleftrightarrow{\Gamma}^{r_2} \right)^{-1/2} \\ &\quad \times \int d\vec{u} \, \Theta \left(-\vec{u} \cdot \hat{q} + \vec{B} \cdot \hat{q} - w_{r_1 r_2} \right) \left(\vec{u} \cdot \hat{q} - \vec{B} \cdot \hat{q} + w_{r_1 r_2} \right) \\ &\quad \times \exp \left(-\vec{u} \cdot \left(\overleftrightarrow{\Gamma}^{r_1-1} + \overleftrightarrow{\Gamma}^{r_2-1} \right)^{-1} \cdot \vec{u} \right) \\ &\quad \times \exp \left(\vec{B} \cdot \left(\overleftrightarrow{\Gamma}^{r_1-1} + \overleftrightarrow{\Gamma}^{r_2-1} \right)^{-1} \cdot \vec{B} + \frac{1}{4} \vec{\Lambda} \cdot \left(\overleftrightarrow{\Gamma}^{r_1} + \overleftrightarrow{\Gamma}^{r_2} \right)^{-1} \cdot \vec{\Lambda} - x w_{r_1 r_2} \vec{\Lambda} \cdot \hat{q} \right). \end{aligned} \quad (85)$$

Next, expanding

$$\vec{B} \cdot \left(\overleftrightarrow{\Gamma}^{r_1-1} + \overleftrightarrow{\Gamma}^{r_2-1} \right)^{-1} \cdot \vec{B} + \frac{1}{4} \vec{\Lambda} \cdot \left(\overleftrightarrow{\Gamma}^{r_1} + \overleftrightarrow{\Gamma}^{r_2} \right)^{-1} \cdot \vec{\Lambda} = \frac{1}{4} \vec{\Lambda} \cdot \overleftrightarrow{G}^{r_1 r_2}(x) \cdot \vec{\Lambda} \quad (86)$$

with

$$\begin{aligned} \overleftrightarrow{G}^{r_1 r_2}(x) &= \overleftrightarrow{\Gamma}^{r_1-1} + 2 \left(\overleftrightarrow{\Gamma}^{r_1} + \overleftrightarrow{\Gamma}^{r_2} \right)^{-1} - x \left(\overleftrightarrow{\Gamma}^{r_1-1} \cdot \hat{q} \hat{q} + \hat{q} \overleftrightarrow{\Gamma}^{r_1-1} \cdot \hat{q} \right) + x^2 X_{r_1 r_2}^2 \hat{q} \hat{q} \\ X_{r_1 r_2}^2 &= \hat{q} \cdot \left(\overleftrightarrow{\Gamma}^{r_1-1} + \overleftrightarrow{\Gamma}^{r_2-1} \right) \cdot \hat{q} \end{aligned} \quad (87)$$

gives

$$\begin{aligned} \tilde{Z}^{r_1 r_2}(x) &= -2 \det \left(\overleftrightarrow{\Gamma}^{r_1} \overleftrightarrow{\Gamma}^{r_2} \right)^{1/2} \pi^{-D/2} \det \left(\overleftrightarrow{\Gamma}^{r_1} + \overleftrightarrow{\Gamma}^{r_2} \right)^{-1/2} \\ &\quad \times \int d\vec{u} \, \Theta \left(-\vec{u} \cdot \hat{q} + \vec{B} \cdot \hat{q} - w_{r_1 r_2} \right) \left(\vec{u} \cdot \hat{q} - \vec{B} \cdot \hat{q} + w_{r_1 r_2} \right) \\ &\quad \times \exp \left(-\vec{u} \cdot \left(\overleftrightarrow{\Gamma}^{r_1-1} + \overleftrightarrow{\Gamma}^{r_2-1} \right)^{-1} \cdot \vec{u} \right) \exp \left(\frac{1}{4} \vec{\Lambda} \cdot \overleftrightarrow{G}^{r_1 r_2}(x) \cdot \vec{\Lambda} - x w_{r_1 r_2} \vec{\Lambda} \cdot \hat{q} \right). \end{aligned} \quad (88)$$

The velocity integral is performed using

$$\begin{aligned} &\int d\vec{u} \, \Theta \left(-\vec{u} \cdot \hat{q} + \vec{B} \cdot \hat{q} - w_{r_1 r_2} \right) \left(\vec{u} \cdot \hat{q} - \vec{B} \cdot \hat{q} + w_{r_1 r_2} \right) \exp \left(-\vec{u} \cdot \overleftrightarrow{M} \cdot \vec{u} \right) \\ &= \det \left(\overleftrightarrow{M} \right)^{-1/2} \int d\vec{u}' \, \Theta \left(-\vec{u}' \cdot \overleftrightarrow{M}^{-1/2} \cdot \hat{q} + \vec{B} \cdot \hat{q} - w_{r_1 r_2} \right) \left(\vec{u}' \cdot \overleftrightarrow{M}^{-1/2} \cdot \hat{q} - \vec{B} \cdot \hat{q} + w_{r_1 r_2} \right) \exp \left(-u'^2 \right) \\ &= \det \left(\overleftrightarrow{M} \right)^{-1/2} \pi^{\frac{D-1}{2}} \left| \overleftrightarrow{M}^{-1/2} \cdot \hat{q} \right| \int_{-\infty}^{\frac{\vec{B} \cdot \hat{q} - w_{r_1 r_2}}{\left| \overleftrightarrow{M}^{-1/2} \cdot \hat{q} \right|}} \left(u' - \frac{\vec{B} \cdot \hat{q} - w_{r_1 r_2}}{\left| \overleftrightarrow{M}^{-1/2} \cdot \hat{q} \right|} \right) \exp \left(-u'^2 \right) du' \\ &= -\frac{1}{2} \det \left(\overleftrightarrow{M} \right)^{-1/2} \pi^{\frac{D}{2}} \left| \overleftrightarrow{M}^{-1/2} \cdot \hat{q} \right| F_1 \left(\frac{w_{r_1 r_2} - \vec{B} \cdot \hat{q}}{\left| \overleftrightarrow{M}^{-1/2} \cdot \hat{q} \right|} \right) \end{aligned} \quad (89)$$

where

$$F_n(x) \equiv -\frac{2}{\sqrt{\pi}} \int_{-\infty}^{-x} (u' + x) \exp \left(-u'^2 \right) du' \quad (90)$$

so that

$$\begin{aligned} F_0(x) &= \operatorname{erf}(x) - 1 \\ F_1(x) &= \frac{1}{\sqrt{\pi}} e^{-x^2} + x (\operatorname{erf}(x) - 1) \end{aligned} \quad (91)$$

Noting that $\left| \left(\overleftrightarrow{\Gamma}^{r_1-1} + \overleftrightarrow{\Gamma}^{r_2-1} \right)^{1/2} \cdot \hat{q} \right| = X_{r_1 r_2}$ and $\det \left(\left(\overleftrightarrow{\Gamma}^{r_1-1} + \overleftrightarrow{\Gamma}^{r_2-1} \right)^{-1} \right)^{-1/2} = \det \left(\overleftrightarrow{\Gamma}^{r_1} \right)^{-1/2} \det \left(\overleftrightarrow{\Gamma}^{r_2} \right)^{-1/2} \det \left(\overleftrightarrow{\Gamma}^{r_1} + \overleftrightarrow{\Gamma}^{r_2} \right)^{1/2}$ one has that

$$\tilde{Z}^{r_1 r_2}(x) = F_1 \left(\frac{w_{r_1 r_2} - \vec{B} \cdot \hat{q}}{\left| \overleftrightarrow{M}^{-1/2} \cdot \hat{q} \right|} \right) \exp \left(\frac{1}{4} \vec{\Lambda} \cdot \overleftrightarrow{G}^{r_1 r_2}(x) \cdot \vec{\Lambda} - x w_{r_1 r_2} \vec{\Lambda} \cdot \hat{q} \right). \quad (92)$$

The final result is then summarized as

$$Z_{[n]}^{r_1 r_2} = \frac{1}{2} \det \left(\overleftrightarrow{\Gamma}^{r_1} \overleftrightarrow{\Gamma}^{r_2} \right)^{-1/2} \sigma_{r_1 r_2}^{D-1} \int d\hat{q} \left(\prod_{j=1}^n \sigma_{r_1 r_2} \hat{q}_{i_j} \right) \left[\tilde{Z}^{r_1 r_2} \left((1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} \right) - \tilde{Z}^{r_1 r_2}(0) \right] \quad (93)$$

with

$$\begin{aligned} \tilde{Z}^{r_1 r_2}(x) &= X_{r_1 r_2} F_1 \left(\frac{2w_{r_1 r_2} + \vec{\Lambda} \cdot \overleftrightarrow{\Gamma}^{r_1-1} \cdot \hat{q}_{12}}{2X_{r_1 r_2}} - \frac{1}{2} x \left(\vec{\Lambda} \cdot \hat{q} \right) X_{r_1 r_2} \right) \\ &\quad \times \exp \left(\frac{1}{4} \vec{\Lambda} \cdot \overleftrightarrow{G}^{r_1 r_2}(x) \cdot \vec{\Lambda} - x w_{r_1 r_2} \vec{\Lambda} \cdot \hat{q} \right) \\ X_{r_1 r_2} &= \sqrt{\hat{q} \cdot \left(\overleftrightarrow{\Gamma}^{r_1-1} + \overleftrightarrow{\Gamma}^{r_2-1} \right) \cdot \hat{q}} \\ \overleftrightarrow{G}^{r_1 r_2}(x) &= \overleftrightarrow{\Gamma}^{r_1-1} + 2 \left(\overleftrightarrow{\Gamma}^{r_1} + \overleftrightarrow{\Gamma}^{r_2} \right)^{-1} - 2x \overleftrightarrow{\Gamma}^{r_1-1} \cdot \hat{q} \hat{q} + x^2 X_{r_1 r_2}^2 \hat{q} \hat{q} \\ w_{r_1 r_2} &= (\vec{u}^{r_1}(\vec{q}_1) - \vec{u}^{r_2}(\vec{q}_1 - \sigma_{r_1 r_2} \hat{q})) \cdot \hat{q}. \end{aligned} \quad (94)$$

In this calculation, it has been implicitly assumed that $\overleftrightarrow{\Gamma}^{r_1}$, $\overleftrightarrow{\Gamma}^{r_2}$ and n_{r_1} , n_{r_2} are independent of position. However, this assumption is unnecessary and the same result applies for spatially dependent quantities provided the substitutions

$$\begin{aligned} \overleftrightarrow{\Gamma}^{r_1} &\rightarrow \overleftrightarrow{\Gamma}^{r_1}(\vec{q}_1) \\ \overleftrightarrow{\Gamma}^{r_2} &\rightarrow \overleftrightarrow{\Gamma}^{r_2}(\vec{q}_1 - \sigma_{r_1 r_2} \hat{q}) \end{aligned} \quad (95)$$

etc., are made and quantities involving \hat{q} are brought under the integrals.

EVALUATION OF THE COLLISION INTEGRALS

In this Appendix, the generating function is used to evaluate the coefficients of the moment expansions.

Evaluation of $E_{i_1 i_2}^{r_1 r_2}$

We need

$$E_{i_1 i_2}^{r_1 r_2} = 2 \det \left(\overleftrightarrow{\Gamma}^{r_1} \overleftrightarrow{\Gamma}^{r_2} \right)^{1/2} \lim_{\vec{\Lambda} \rightarrow 0} \frac{\partial^2}{\partial \Lambda_{i_1} \partial \Lambda_{i_2}} \left[\tilde{Z}^{r_1 r_2}(x) - \tilde{Z}^{r_1 r_2}(0) \right] \quad (96)$$

which is evaluated using

$$\begin{aligned} \lim_{\vec{\Lambda} \rightarrow 0} \frac{\partial^2}{\partial \Lambda_{i_1} \partial \Lambda_{i_2}} \tilde{Z}^{r_1 r_2}(x) &= X_{r_1 r_2} F_1'' \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \left(\frac{\overleftrightarrow{\Gamma}^{r_1-1} \cdot \hat{q}}{2X_{r_1 r_2}} \right)_{i_1} \left(\frac{\overleftrightarrow{\Gamma}^{r_1-1} \cdot \hat{q}}{2X_{r_1 r_2}} \right)_{i_2} + X_{r_1 r_2} F_1 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \frac{1}{2} G_{i_1 i_2}^{r_1 r_2}(x) \\ &\quad - \frac{1}{2} x X_{r_1 r_2} \left[\frac{1}{2} F_1'' \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) + \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) F_1' \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \right] \left[\left(\overleftrightarrow{\Gamma}^{r_1-1} \cdot \hat{q} \right)_{i_1} \hat{q}_{i_2} + \left(\overleftrightarrow{\Gamma}^{r_1-1} \cdot \hat{q} \right)_{i_2} \hat{q}_{i_1} \right] \\ &\quad + x^2 X_{r_1 r_2}^3 \left[\left(\frac{1}{2} \right)^2 F_1'' \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) + \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) F_1' \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) + \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right)^2 F_1 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \right] \hat{q}_{i_1} \hat{q}_{i_2} \end{aligned} \quad (97)$$

Substituting the explicit expression for $\overleftrightarrow{G}(x)$ gives

$$\begin{aligned} \lim_{\overline{\Lambda} \rightarrow 0} \frac{\partial^2}{\partial \Lambda_{i_1} \partial \Lambda_{i_2}} \left[\tilde{Z}^{r_1 r_2}(x) - \tilde{Z}^{r_1 r_2}(0) \right] &= \tilde{Z}^{r_1 r_2} \left(x, \frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \\ \tilde{Z}^{r_1 r_2}(x, y) &= -\frac{1}{2} x X_{r_1 r_2} \left[\frac{1}{2} F_1''(y) + y F_1'(y) + F_1(y) \right] \left[\left(\overleftrightarrow{\Gamma}^{r_1-1} \cdot \hat{q} \right)_{i_1} \hat{q}_{i_2} + \left(\overleftrightarrow{\Gamma}^{r_1-1} \cdot \hat{q} \right)_{i_2} \hat{q}_{i_1} \right] \\ &\quad + x^2 X_{r_1 r_2}^3 \left[\left(\frac{1}{2} \right)^2 F_1''(y) + y F_1'(y) + y^2 F_1(y) + \frac{1}{2} F_1(y) \right] \hat{q}_{i_1} \hat{q}_{i_2} \end{aligned} \quad (98)$$

so that, using $F_n'(x) = n F_{n-1}(x) + \delta_{n0} 2(F_1(x) - x F_0(x))$, one has

$$\begin{aligned} \tilde{Z}^{r_1 r_2}(x, y) &= -x X_{r_1 r_2} F_1(y) \left[\left(\overleftrightarrow{\Gamma}^{r_1-1} \cdot \hat{q} \right)_{i_1} \hat{q}_{i_2} + \left(\overleftrightarrow{\Gamma}^{r_1-1} \cdot \hat{q} \right)_{i_2} \hat{q}_{i_1} \right] \\ &\quad + \frac{1}{2} x^2 X_{r_1 r_2}^3 [y F_0(y) + (2y^2 + 2) F_1(y)] \hat{q}_{i_1} \hat{q}_{i_2} \end{aligned} \quad (99)$$

and

$$\begin{aligned} E_{i_1 i_2}^{r_1 r_2} &= -\sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} \int d\hat{q} X_{r_1 r_2} F_1 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \left[\left(\overleftrightarrow{\Gamma}^{r_1-1} \cdot \hat{q} \right)_{i_1} \hat{q}_{i_2} + \left(\overleftrightarrow{\Gamma}^{r_1-1} \cdot \hat{q} \right)_{i_2} \hat{q}_{i_1} \right] \\ &\quad + \frac{1}{2} \sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2})^2 \left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \right)^2 \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} X_{r_1 r_2}^3 \left[\left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) F_0 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) + F_1 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \left(2 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right)^2 + 2 \right) \right]. \end{aligned} \quad (100)$$

Evaluation of $B_{i_1 i_2}^{r_1 r_2}$

This follows by taking the appropriate limit of $E_{i_1 i_2}^{r_1 r_2}$:

$$\begin{aligned} B_{i_1 i_2}^{r_1 r_2} &= \frac{m_{r_1}}{2k_B T_{r_1}} \lim_{\overleftrightarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x} \overleftrightarrow{1}} E_{i_1 i_2}^{r_1 r_2} \\ &= -2\sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} Y_{r_1 r_2} \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} F_1 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \\ &\quad + \frac{1}{4} \sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2})^2 \left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \right)^2 Y_{r_1 r_2}^3 \frac{m_{r_1}}{k_B T_{r_1}} \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} \left[\left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right) F_0 \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right) + F_1 \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right) \left(2 \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right)^2 + 2 \right) \right] \end{aligned} \quad (101)$$

with

$$Y_{r_1 r_2} = \sqrt{2 \frac{k_B T_{r_1}}{m_{r_1}} + 2 \frac{k_B T_{r_2}}{m_{r_2}}}. \quad (102)$$

Evaluation of $D_{i_1 i_2, j_1 j_2}^{r_1 r_2}$

We need to evaluate $D_{i_1 i_2, j_1 j_2}^{r_1 r_2} = -\frac{m_{r_1}}{2k_B T_{r_1}} \frac{m_{r_2}}{k_B T_{r_2}} \lim_{\overleftrightarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x} \overleftrightarrow{1}} \frac{\partial}{\partial \Gamma_{j_1 j_2}^{r_2}} E_{i_1 i_2}^{r_1 r_2}$

$$\begin{aligned}
D_{i_1 i_2, j_1 j_2}^{r_1 r_2} &= -\frac{m_{r_1}}{2k_B T_{r_1}} \frac{m_{r_2}}{k_B T_{r_2}} \lim_{\overleftarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x} \overleftarrow{\Gamma}} \frac{\partial}{\partial \Gamma_{j_1 j_2}^{r_2}} \det \left(\overleftarrow{\Gamma}^{r_1} \overleftarrow{\Gamma}^{r_2} \right)^{1/2} E_{i_1 i_2}^{r_1 r_2} \\
&= \sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} \frac{m_{r_1}}{2k_B T_{r_1}} \frac{m_{r_2}}{k_B T_{r_2}} \\
&\quad \times \lim_{\overleftarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x} \overleftarrow{\Gamma}} \frac{\partial}{\partial \Gamma_{j_1 j_2}^{r_2}} \int d\hat{q} X_{r_1 r_2} F_1 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \left[\left(\overleftarrow{\Gamma}^{r_1-1} \cdot \hat{q} \right)_{i_1} \hat{q}_{i_2} + \left(\overleftarrow{\Gamma}^{r_1-1} \cdot \hat{q} \right)_{i_2} \hat{q}_{i_1} \right] \\
&\quad - \frac{1}{4} \sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2})^2 \left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \right)^2 \frac{m_{r_1}}{k_B T_{r_1}} \frac{m_{r_2}}{k_B T_{r_2}} \\
&\quad \times \lim_{\overleftarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x} \overleftarrow{\Gamma}} \frac{\partial}{\partial \Gamma_{j_1 j_2}^{r_2}} \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} X_{r_1 r_2}^3 \left[\left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) F_0 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) + F_1 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \left(2 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right)^2 + 2 \right) \right]
\end{aligned} \tag{103}$$

Then, using

$$\lim_{\overleftarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x} \overleftarrow{\Gamma}} \frac{\partial}{\partial \Gamma_{j_1 j_2}^{r_2}} X_{r_1 r_2} = -\frac{1}{2} Y_{r_1 r_2}^{-1} \left(\frac{2k_B T_{r_2}}{m_{r_2}} \right)^2 \hat{q}_{j_1} \hat{q}_{j_2} \tag{104}$$

gives

$$\begin{aligned}
D_{i_1 i_2, j_1 j_2}^{r_1 r_2} &= \sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} \frac{m_{r_1}}{2k_B T_{r_1}} \frac{m_{r_2}}{k_B T_{r_2}} \frac{4k_B T_{r_1}}{m_{r_1}} \\
&\quad \times \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} \hat{q}_{i'_1} \hat{q}_{i'_2} \left(-\frac{1}{2} Y_{r_1 r_2}^{-1} \left(\frac{2k_B T_{r_2}}{m_{r_2}} \right)^2 \right) \left(\lim_{\overleftarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x} \overleftarrow{\Gamma}} \frac{\partial}{\partial X_{r_1 r_2}} X_{r_1 r_2} F_1 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \right) \\
&\quad - \frac{1}{4} \sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2})^2 \left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \right)^2 \frac{m_{r_1}}{k_B T_{r_1}} \frac{m_{r_2}}{k_B T_{r_2}} \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} \hat{q}_{j_1} \hat{q}_{j_2} \left(-\frac{1}{2} Y_{r_1 r_2}^{-1} \left(\frac{2k_B T_{r_2}}{m_{r_2}} \right)^2 \right) \\
&\quad \times \left(\lim_{\overleftarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x} \overleftarrow{\Gamma}} \frac{\partial}{\partial X_{r_1 r_2}} X_{r_1 r_2}^3 \left[\left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) F_0 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) + F_1 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \left(2 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right)^2 + 2 \right) \right] \right)
\end{aligned} \tag{105}$$

Using

$$\begin{aligned}
\frac{\partial}{\partial X} X F_1 \left(\frac{w}{X} \right) &= F_1 \left(\frac{w}{X} \right) - \left(\frac{w}{X} \right) F_0 \left(\frac{w}{X} \right) \\
\frac{\partial}{\partial X} X^3 \left[\left(\frac{w}{X} \right) F_0 \left(\frac{w}{X} \right) + F_1 \left(\frac{w}{X} \right) \left(2 \left(\frac{w}{X} \right)^2 + 2 \right) \right] &= 6X^2 F_1 \left(\frac{w}{X} \right)
\end{aligned} \tag{106}$$

gives

$$\begin{aligned}
D_{i_1 i_2, j_1 j_2}^{r_1 r_2} &= -4\sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} Y_{r_1 r_2}^{-1} \left(\frac{k_B T_{r_2}}{m_{r_2}} \right) \\
&\quad \times \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} \hat{q}_{j_1} \hat{q}_{j_2} \left(F_1 \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right) - \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right) F_0 \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right) \right) \\
&\quad + 3\sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2})^2 \left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \right)^2 \frac{m_{r_1}}{k_B T_{r_1}} \left(\frac{k_B T_{r_2}}{m_{r_2}} \right) Y_{r_1 r_2} \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} \hat{q}_{j_1} \hat{q}_{j_2} F_1 \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right).
\end{aligned} \tag{107}$$

Evaluation of $C_{i_1 i_2, j_1 j_2}^{r_1 r_2}$

This calculation is very similar to the preceding one. Noting that in the previous calculation we had

$$\left(\frac{m_{r_1}}{k_B T_{r_1}} \right) \left(\frac{m_{r_2}}{k_B T_{r_2}} \right) \lim_{\overleftarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x} \overleftarrow{\Gamma}} \frac{\partial}{\partial \Gamma_{j_1 j_2}^{r_2}} X_{r_1 r_2} = -2Y_{r_1 r_2}^{-1} \hat{q}_{j_1} \hat{q}_{j_2} \left(\frac{m_{r_1}}{k_B T_{r_1}} \right) \left(\frac{k_B T_{r_2}}{m_{r_2}} \right) \tag{108}$$

whereas from the definition

$$C_{i_1 i_2, j_1 j_2}^{r_1 r_2} = -\frac{1}{2} \left(\frac{m_{r_1}}{k_B T_{r_1}} \right)^2 \lim_{\overleftrightarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x}} \overleftrightarrow{\Gamma} \frac{\partial}{\partial \Gamma_{j_1 j_2}^{r_1}} E_{i_1 i_2}^{r_1 r_2} \quad (109)$$

the present calculation will require

$$\left(\frac{m_{r_1}}{k_B T_{r_1}} \right)^2 \lim_{\overleftrightarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x}} \overleftrightarrow{\Gamma} \frac{\partial}{\partial \Gamma_{j_1 j_2}^{r_1}} X_{r_1 r_2} = -2Y_{r_1 r_2}^{-1} \hat{q}_{j_1} \hat{q}_{j_2} \quad (110)$$

we can immediately write

$$\begin{aligned} C_{i_1 i_2, j_1 j_2}^{r_1 r_2} &= \left(\frac{m_{r_2}}{k_B T_{r_2}} \right) \left(\frac{k_B T_{r_1}}{m_{r_1}} \right) D_{i_1 i_2, j_1 j_2}^{r_1 r_2} \\ &+ \frac{1}{2} \left(\frac{m_{r_1}}{k_B T_{r_1}} \right)^2 \sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} Y_{r_1 r_2} \\ &\times \int d\hat{q} F_1 \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right) \lim_{\overleftrightarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x}} \overleftrightarrow{\Gamma} \frac{\partial}{\partial \Gamma_{j_1 j_2}^{r_1}} \left[\left(\overleftrightarrow{\Gamma}^{r_1-1} \cdot \hat{q} \right)_{i_1} \hat{q}_{i_2} + \left(\overleftrightarrow{\Gamma}^{r_1-1} \cdot \hat{q} \right)_{i_2} \hat{q}_{i_1} \right]. \end{aligned} \quad (111)$$

Using

$$\lim_{\overleftrightarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x}} \overleftrightarrow{\Gamma} \frac{\partial}{\partial \Gamma_{j_1 j_2}^{r_1}} \overleftrightarrow{\Gamma}^{r_1-1}_{i_1 i'_1} = - \lim_{\overleftrightarrow{\Gamma}^x \rightarrow \frac{m_x}{2k_B T_x}} \overleftrightarrow{\Gamma}^{r_1-1}_{i_1 j_1} \overleftrightarrow{\Gamma}^{r_1-1}_{j_2 i'_1} = - \left(\frac{m_1}{2k_B T_1} \right)^{-2} \delta_{i_1 j_1} \delta_{j_2 i'_1} \quad (112)$$

gives

$$\begin{aligned} C_{i_1 i_2, j_1 j_2}^{r_1 r_2} &= \left(\frac{m_{r_2}}{k_B T_{r_2}} \right) \left(\frac{k_B T_{r_1}}{m_{r_1}} \right) D_{i_1 i_2, j_1 j_2}^{r_1 r_2} \\ &- 2\sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} Y_{r_1 r_2} \int d\hat{q} (\delta_{i_1 j_1} \hat{q}_{i_2} \hat{q}_{j_2} + \delta_{i_2 j_1} \hat{q}_{i_1} \hat{q}_{j_2}) F_1 \left(\frac{w_{r_1 r_2}}{Y_{r_1 r_2}} \right) \\ &[\delta_{i_1 j_1} \hat{q}_{j_2} \hat{q}_{i_2} + \delta_{i_2 j_1} \hat{q}_{j_2} \hat{q}_{i_1}] \Gamma_{j_1 j_2}^{r_1-1} \end{aligned} \quad (113)$$

Evaluation of the pressure

Recall that the collisional part of the pressure is given by

$$P_{i_1 i_2}^V = \frac{1}{4} \sum_{r_1 r_2} n_{r_1} n_{r_2} \chi_{r_1 r_2} \det \left(\overleftrightarrow{\Gamma}^{r_1} \overleftrightarrow{\Gamma}^{r_2} \right)^{1/2} m_{r_1} \lim_{\overleftrightarrow{\Lambda} \rightarrow \vec{0}} \frac{\partial}{\partial \Lambda_{i_2}} Z_{i_1}^{r_1 r_2}. \quad (114)$$

Starting with

$$\lim_{\overleftrightarrow{\Lambda} \rightarrow \vec{0}} \frac{\partial}{\partial \Lambda_{i_2}} \tilde{Z}^{r_1 r_2}(x) = X_{r_1 r_2} F_1' \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \left(\frac{\overleftrightarrow{\Gamma}^{r_1-1} \cdot \hat{q}_{12}}{2X_{r_1 r_2}} - \frac{1}{2} x X_{r_1 r_2} \hat{q} \right)_{i_2} + X_{r_1 r_2} F_1 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) (-x w_{r_1 r_2} \hat{q}_{i_2}) \quad (115)$$

gives

$$\lim_{\overleftrightarrow{\Lambda} \rightarrow \vec{0}} \frac{\partial}{\partial \Lambda_{i_2}} \left[\tilde{Z}^{r_1 r_2} \left(x; \overleftrightarrow{\Gamma}^{r_1}, \overleftrightarrow{\Gamma}^{r_2}, \overleftrightarrow{\Lambda} \right) - \tilde{Z}^{r_1 r_2} \left(0; \overleftrightarrow{\Gamma}^{r_1}, \overleftrightarrow{\Gamma}^{r_2}, \overleftrightarrow{\Lambda} \right) \right] = -\frac{1}{2} \hat{q}_{i_2} x X_{r_1 r_2}^2 \left(F_1' \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) + 2 \frac{w_{r_1 r_2}}{X_{r_1 r_2}} F_1 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \right) \quad (116)$$

and

$$P_{i_1 i_2}^V = -\frac{1}{8} \sum_{r_1 r_2} n_{r_1} n_{r_2} \sigma_{r_1 r_2}^D \chi_{r_1 r_2} (1 + \alpha_{r_1 r_2}) \mu_{r_1 r_2} \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} X_{r_1 r_2}^2 \left(F_0 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) + 2 \frac{w_{r_1 r_2}}{X_{r_1 r_2}} F_1 \left(\frac{w_{r_1 r_2}}{X_{r_1 r_2}} \right) \right). \quad (117)$$

SME IN THE BOLTZMANN LIMIT

The Boltzmann limit of the coefficients needed for the SME are

$$\begin{aligned}
B_{i_1 i_2}^{r_1 r_2} &= -\sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} \frac{1}{\sqrt{\pi}} Y_{r_1 r_2} \left[2 - \frac{1}{2} (1 + \alpha_{r_1 r_2}) \left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \right) Y_{r_1 r_2}^2 \frac{m_{r_1}}{k_B T_{r_1}} \right] \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} \\
C_{i_1 i_2, i'_1 i'_2}^{r_1 r_2} &= \frac{T_{r_1}}{T_{r_2}} \frac{m_{r_2}}{m_{r_1}} D_{i_1 i_2, j_1 j_2}^{r_1 r_2} - 2\sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} Y_{r_1 r_2} \frac{1}{\sqrt{\pi}} \int d\hat{q} (\delta_{i_1 i'_1} \hat{q}_{i_2} \hat{q}_{i'_2} + \delta_{i_2 i'_1} \hat{q}_{i_1} \hat{q}_{i'_2}) \\
D_{i_1 i_2, i'_1 i'_2}^{r_1 r_2} &= -4\sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} Y_{r_1 r_2}^{-1} \left(\frac{k_B T_{r_2}}{m_{r_2}} \right) \frac{1}{\sqrt{\pi}} \left[1 - \frac{3}{4} (1 + \alpha_{r_1 r_2}) \left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \right) \frac{m_{r_1}}{k_B T_{r_1}} Y_{r_1 r_2}^2 \right] \int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} \hat{q}_{i'_1} \hat{q}_{i'_2}
\end{aligned} \tag{118}$$

where

$$Y_{r_1 r_2} = \sqrt{2 \frac{k_B T_{r_1}}{m_{r_1}} + 2 \frac{k_B T_{r_2}}{m_{r_2}}}. \tag{119}$$

Using the elementary integrals

$$\begin{aligned}
\int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} &= \frac{S_D}{D} \delta_{i_1 i_2} \\
\int d\hat{q} \hat{q}_{i_1} \hat{q}_{i_2} \hat{q}_{i'_1} \hat{q}_{i'_2} &= \frac{S_D}{D^2 + 2D} (\delta_{i_1 i_2} \delta_{i'_1 i'_2} + \delta_{i_1 i'_1} \delta_{i_2 i'_2} + \delta_{i_1 i'_2} \delta_{i_2 i'_1})
\end{aligned} \tag{120}$$

where the area of a sphere in D dimensions is

$$S_D = \frac{2\pi^{D/2}}{\Gamma(D/2)} \tag{121}$$

gives

$$\begin{aligned}
B_{i_1 i_2}^{r_1 r_2} &= B^{r_1 r_2} \delta_{i_1 i_2} \\
C_{i_1 i_2, i'_1 i'_2}^{r_1 r_2} &= \frac{T_{r_1}}{T_{r_2}} \frac{m_{r_2}}{m_{r_1}} D_{i_1 i_2, j_1 j_2}^{r_1 r_2} + C^{r_1 r_2} (\delta_{i_1 i'_1} \delta_{i_2 i'_2} + \delta_{i_2 i'_1} \delta_{i_1 i'_2}) \\
D_{i_1 i_2, i'_1 i'_2}^{r_1 r_2} &= D^{r_1 r_2} (\delta_{i_1 i_2} \delta_{i'_1 i'_2} + \delta_{i_1 i'_1} \delta_{i_2 i'_2} + \delta_{i_1 i'_2} \delta_{i_2 i'_1}) \\
B^{r_1 r_2} &= -\sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} \frac{1}{\sqrt{\pi}} Y_{r_1 r_2} \left[2 - \frac{1}{2} (1 + \alpha_{r_1 r_2}) \left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \right) Y_{r_1 r_2}^2 \frac{m_{r_1}}{k_B T_{r_1}} \right] \frac{S_D}{D} \\
C^{r_1 r_2} &= -2\sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} Y_{r_1 r_2} \frac{1}{\sqrt{\pi}} \frac{S_D}{D} \\
D^{r_1 r_2} &= -4\sigma_{r_1 r_2}^{D-1} (1 + \alpha_{r_1 r_2}) \frac{\mu_{r_1 r_2}}{m_{r_1}} Y_{r_1 r_2}^{-1} \left(\frac{k_B T_{r_2}}{m_{r_2}} \right) \frac{1}{\sqrt{\pi}} \left[1 - \frac{3}{4} (1 + \alpha_{r_1 r_2}) \left(\frac{\mu_{r_1 r_2}}{m_{r_1}} \right) \frac{m_{r_1}}{k_B T_{r_1}} Y_{r_1 r_2}^2 \right] \frac{S_D}{D^2 + 2D}
\end{aligned} \tag{122}$$

so that

$$\begin{aligned}
D_{i_1 i_2, i'_1 i'_2}^{r_1 r_2} A_{i'_1 i'_2}^{r_2} &= 2D^{r_1 r_2} A_{i_1 i_2}^{r_2} \\
C_{i_1 i_2, i'_1 i'_2}^{r_1 r_2} A_{i'_1 i'_2}^{r_1} &= 2 \frac{T_{r_1}}{T_{r_2}} \frac{m_{r_2}}{m_{r_1}} D^{r_1 r_2} A_{i_1 i_2}^{r_1} + 2 C^{r_1 r_2} A_{i_1 i_2}^{r_1}.
\end{aligned} \tag{123}$$

Then, the moment equations become

$$\begin{aligned}
2a A_{xy}^{r_1} \delta_{ix} &= n B^{r_1} + n \sum_{r_2} D^{r_1 r_2} A_{ii}^{r_2} + n \mathcal{H}^{r_1} A_{ii}^{r_1} \\
a + a A_{yy}^{r_1} &= n \sum_{r_2} D^{r_1 r_2} A_{xy}^{r_2} + n \mathcal{H}^{r_1} A_{xy}^{r_1}
\end{aligned} \tag{124}$$

where

$$\begin{aligned}
B^{r_1} &= \sum_{r_2} B^{r_1 r_2} \\
\mathcal{H}^{r_1} &= \sum_{r_2} \left[\frac{T_{r_1}}{T_{r_2}} \frac{m_{r_2}}{m_{r_1}} D^{r_1 r_2} + C^{r_1 r_2} \right]
\end{aligned}$$

Clearly all $A_{ii}^{r_1}$ are equal for $i \neq x$ and the tracelessness means that $A_{xx}^{r_1} = -(D-1)A_{yy}^{r_1}$. Then

$$\begin{aligned}\mathcal{H}^{r_1} A_{yy}^{r_1} &= -\mathcal{B}^{r_1} - \sum_{r_2} D^{r_1 r_2} A_{yy}^{r_2} \\ 2a A_{xy}^{r_1} &= n D \mathcal{B}^{r_1} \\ a^2 &= n^2 D \frac{\sum_{r_2} D^{r_1 r_2} \mathcal{B}^{r_2} + \mathcal{H}^{r_1} \mathcal{B}^{r_1}}{2 + 2A_{yy}^{r_1}} \\ T &= \sum_r x_r T_r\end{aligned}\tag{125}$$

which constitute $n + n + n + 1 = 3n + 1$ equations for the unknowns $\{A_{yy}^{r_1}, A_{xy}^{r_1}, T_{r_1}\}_{r_1=1}^n, a$. For a one-component fluid, one has that

$$\begin{aligned}Y_{r_1 r_2} &\rightarrow 2\sqrt{\frac{k_B T}{m}} \\ \mathcal{B}^{r_1} &\rightarrow -(1-\alpha^2) \frac{S_D}{D} \sigma^{D-1} \sqrt{\frac{k_B T}{\pi m}} \\ D^{r_1 r_1} &\rightarrow (1+\alpha) \frac{1+3\alpha}{2} \frac{S_D}{D^2+2D} \sigma^{D-1} \sqrt{\frac{k_B T}{\pi m}} \\ \mathcal{H}^{r_1} &\rightarrow (1+\alpha) \left(\frac{1+3\alpha}{2} \frac{1}{D+2} - 2 \right) \frac{S_D}{D} \sigma^{D-1} \sqrt{\frac{k_B T}{\pi m}}\end{aligned}\tag{126}$$

and eqs.(125) can be solved explicitly with the result that

$$\begin{aligned}A_{yy} &= -\frac{(1-\alpha)(D+2)}{3-3\alpha+2D} \\ a^* A_{xy}^{r_1} &= -n^* (1-\alpha^2) \frac{S_D}{2\sqrt{\pi}} \\ a^* &= n^* \frac{S_D}{D} \sqrt{\frac{D}{2\pi}} (3-3\alpha+2D) \sqrt{\frac{(1-\alpha^2)(1+\alpha)}{(D+2)(D+1+\alpha(D-1))}}\end{aligned}\tag{127}$$

where

$$\begin{aligned}a^* &= a \sqrt{\frac{m \sigma^2}{k_B T}} \\ n^* &= n \sigma^D.\end{aligned}\tag{128}$$

Recall that in this approximation

$$P_{ij}^K = nk_B T \left(\vec{1} + \overleftrightarrow{A}^r \right)\tag{129}$$

so that

$$\begin{aligned}P_{yy} &= nk_B T \left(\frac{1+D+(D-1)\alpha}{3+2D-3\alpha} \right) \\ P_{xy} &= -nk_B T \left[\frac{1}{(3-3\alpha+2D)} \sqrt{D \left(\frac{D+2}{2} \right) (1-\alpha)(D+1+\alpha(D-1))} \right] \\ \eta &= -P_{xy}/a = \eta_0 \left(\frac{1}{3-3\alpha+2D} \right)^2 \frac{4D(D+1+\alpha(D-1))}{(1+\alpha)}\end{aligned}\tag{130}$$

with

$$\eta_0 = \sigma^{1-D} \sqrt{m k_B T} \left(\frac{(D+2) \Gamma(D/2)}{8\pi^{(D-1)/2}} \right).\tag{131}$$

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